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Niagara River Mussel Biomonitoring Program 2003



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Niagara River Mussel Biomonitoring Program, 2003

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FOREWORD

The data generated by the 2003 Niagara River Biomonitoring Survey augment other federal and provincial Niagara River Toxics Management Plan programs by providing information on contaminants in the river between Fort Erie and Niagara-on-the-Lake. The Niagara River mussel biomonitoring survey, conducted by the Ontario Ministry of Environment, has been ongoing since 1980 (Kauss 1987; Kauss and Angelow 1988; Anderson *et al.* 1991; Richman 1992 - 2003).

Information provided by this study is part of an overall program to assess long-term trends in contaminant loadings from selected U.S. and Canadian sources along the Niagara River.

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SUMMARY

Since 1980 the Ontario Ministry of Environment (MOE) has been committed to both routine and specialized biomonitoring of contaminants in the Niagara River using caged mussels (*Elliptio complanata*) as part of Ontario's commitment to the Niagara River Toxic Management Plan. Mussels were deployed on the American as well as the Canadian side of the river. These studies have provided information on suspected contaminant sources and source areas in the river between Fort Erie and Niagara-on-the-Lake (NOTL) (Kauss 1987; Kauss and Angelow 1988; Anderson *et al.* 1991; Richman 1992 - 2003).

In 2003, caged mussels were deployed at five stations on the Canadian side of the river and 29 sites on the American side of the river for 21 days of exposure. Mussels were retrieved after the designated period of deployment from all but two stations on the American side of the river. Cages at these two sites were either vandalized or drifted away from the point of deployment. Additional cages were deployed at one of these sites (Bloody Run Creek) in 2004. All samples were analysed for organochlorine pesticides, total polychlorinated biphenyls (PCBs), chlorinated benzenes, and polycyclic aromatic hydrocarbons (PAHs). Samples from selected sites were analysed for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/PCDF) and polybrominated diphenyl ethers (PBDEs).

Twenty-one day Deployment - Summary of Findings.

The detection of organochlorine pesticides such as p,p'-DDE and hexachlorocyclohexanes (α -HCH, β -HCH and γ -HCH), in mussels deployed along the Canadian and American sides of the Niagara River has always been sporadic which is suggestive of non-point sources or historic residual contamination. The data from 2003 were consistent with previous mussel monitoring surveys. Typically, trace concentrations of p,p'-DDE and/or HCH have been detected in mussels at a few stations (e.g. Frenchmans Creek, Lyons Creek, Cayuga Creek, Gill Creek, Bloody Run Creek).

Ongoing remediation projects have likely contributed to an overall reduction of PCB loadings to the Niagara River and hence, to Lake Ontario. However, the data do suggest that PCB exposure is pervasive in the Niagara River and that PCBs will likely be bioavailable in the future, similar to the continued bioavailability of DDT and its metabolites. Trace concentrations of total PCBs were present in mussels deployed at almost all stations in the survey. This data was consistent with results from the 2000 survey. One control mussel from Balsam Lake also had trace concentrations of total PCBs. Based on Balsam Lake data from the past 25 years of monitoring this was likely due to sample contamination during processing.

The highest total PCB concentrations detected in the 2003 survey were observed in mussels deployed in Lyons Creek (range: 250 to 650 ng/g) which is a site known to be contaminated with PCBs located in Ontario. Remedial actions to clean up contaminated sediment in Lyons Creek are presently being investigated by MOE and are pending the completion of an environmental risk assessment. Lyons Creek flows into the Welland River which discharges to the Niagara River. Previous surveys have not detected PCBs in the Welland River.

The chlorinated compounds most frequently detected in mussel tissue were hexachlorobutadiene (HCBd) (e.g. Occidental Chemical facility, Gill Creek, Bloody Run Creek), 1,2,3,5-tetrachlorobenzene (Occidental Chemical Company, Pettit Flume, Erie Canal, Bloody Run Creek, Two Mile Creek) and 2,3,6-trichlorotoluene (Pettit Flume, Gratwick Riverside Park, mouth of Gill Creek). Hexachlorobenzene (HCB) was identified at most sites but only at trace concentrations. High concentrations of pentachlorobenzene were associated with Bloody Run Creek. Data from Bloody Run Creek suggested that this area was a source of chlorinated benzenes in general to the Niagara River. Trichlorobenzenes and octachlorostyrene were not detected at all in 2003, but have been detected sporadically in previous surveys typically at trace concentrations. In general, 2,3,6- and/or 2,4,5-trichlorotoluene were detected in mussel tissue at several stations although these compounds had not been present in earlier surveys; e.g. Pettit Flume, Gratwick Riverside Park (upstream and downstream), and mouth of Gill Creek. The results were confirmed with laboratory analysts. Presently, it is unclear if they represent an episodic release of the contaminant into the Tonawanda Channel during the period of mussel deployment. Further monitoring is required to identify whether these results were an anomaly for the 2003 survey.

The highest concentrations of PAHs in mussel tissue were present in mussels deployed at the mouths of storm sewers and urban creeks (Cayuga Creek, Two Mile Creek, Pettit Flume, mouth of the sewer discharging to the Niagara River downstream of Superior Lubricant). Concentrations of total PAHs ranged from 620 ng/g to 1,200 ng/g at these sites. Since the sampling sites were located alongside roads and high traffic areas the likely sources of PAHs would be road and surface runoff to storm sewers.

Sediment concentrations of dioxins and furans at NOTL were low (9 pg/g TEQ), and were similar to concentrations measured in 1993 and 1995 (TEQ: 14.8 and 14.2 pg/g respectively).

The TEQs for the sediment samples from Cayuga Creek and Two Mile Creek were 70 and 81 pg/g respectively in 2003 which suggested that the sediments in these areas were contaminated with dioxins and furans. The sediment collected from Gill Creek is of particular interest; in 2000 (the first time the sediment was analysed for dioxins), the TEQ was 103 pg/g similar to concentrations measured in 2003 (119 pg/g). Since the area was remediated due to PCB contamination (i.e. dredged) in 1998, these data suggested the possibility of a recent source of dioxins and furans. Although sediment TEQ concentrations indicated some dioxin/furan contamination, TEQ concentrations in caged mussels were low

for Cayuga Creek and Gill Creek (data for Two Mile Creek were unavailable).

In 2003, sediment collected from the shoreline (bank) of the Niagara River in the vicinity of Bloody Run Creek had extremely high concentrations of dioxins and furans (TEQ; 121,725 pg/g, similar to concentrations measured in 1993. Mussels deployed in the area also had high TEQ concentrations (42 pg/g and 48 pg/g) suggesting that the contaminants were bioavailable and that the area is a source of dioxins to the river.

High concentrations of dioxins and furans were detected in mussels (66 pg/g wet wt.) and sediment (TEQ of 11,383 pg/g dry wt.) collected from the Pettit Flume cove. High concentrations of dioxins and furans were also present in sediment collected from a station just downstream of the cove (TEQ: 2,078 pg/g), suggesting sediment transport from the cove. The contamination outside the cove in 2003 was four times higher than in 2000 (502 pg/g TEQ) implicating the cove as a source of dioxins to the Niagara River. However, the TEQ for mussels deployed outside the cove was low (0.47 pg/g).

Although polybrominated diphenyl ethers (PBDEs) are not listed as priority chemicals within the Niagara River Toxics Management Plan, these compounds have been recently identified as global pollutants and are present in all parts of the environment. Concentrations in the environment are low, but current levels may threaten some wildlife and invertebrates and may exert effects similar to those of PCBs, dioxins and furans (Tanabe 2004). There is concern about the presence of PBDEs since concentrations in the environment have been increasing since the 1970's (Palm *et al.* 2002; Hites 2004; Martin *et al.* 2004). This trend of increasing environmental concentrations has also been noted in the Niagara River by comparing concentrations of PBDEs in suspended sediments collected from the period 1980 to 2002 (Marvin *et al.* 2004). Accordingly, due to the recent analytical method development within the MOE laboratory, PBDEs have been included in the Niagara River mussel monitoring survey to assess their bioavailability in the river.

PBDEs were detected in mussels deployed in the Niagara River. Caged *Elliptio complanata* was a useful bioindicator of PBDEs. The highest concentrations (measured as the total sum of detectable individual PBDE congeners) were present in mussels deployed within tributaries to the American side of the Niagara River (Cayuga Creek 8.6 ng/g wet wt.; Gill Creek 7.2 ng/g; and Two Mile Creek - range 4.0 to 6.3 ng/g). In addition to contributions from the atmosphere (which should be fairly consistent among all sites within the survey), each of these tributaries have storm sewers, hazardous waste site, landfills and industries located nearby the sampling sites that could be potential sources of PBDEs. Total PBDE concentrations were also higher in mussels deployed at all sites in the Tonawanda Channel and Buffalo River (range: 1.7 to 3.3 ng/g) compared with mussels deployed on the Canadian side (Chippawa Channel) and in the lower Niagara (Bloody Run Creek and NOTL). This could be a reflection of the relatively higher degree of industrial activity and larger urban centres within the Tonawanda Channel compared with the other areas. The PBDE congener patterns were similar among the mussels, with BDE-47, -99 and -100 representing the highest concentrations relative to the other detectable congeners.

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INTRODUCTION

Programs initiated by the Canadian and U.S. governments to remediate hazardous waste sites and control discharges from point and non-point sources have resulted in improvements in the water quality of the Niagara River (Niagara River Secretariat 2002). Many of these programs have fallen under the umbrella of the Niagara River Toxics Management Plan (NRTMP) which was part of a binational agreement (first signed in 1987), to improve the environmental quality of the Niagara River. This plan targeted eighteen "priority toxics" for reduction. The most recent water quality trends show a reduction in the concentrations and loads of most of the priority toxics for which there are data (Williams and O'Shea 2003).

The Niagara River was historically contaminated and continues to be contaminated by the discharge of persistent bioaccumulative and toxic chemicals from outfalls and hazardous waste landfills. They include chemicals such as mirex, PCBs (polychlorinated biphenyls), organochlorine pesticides such as γ -HCH (lindane) and chlordane, chlorinated benzenes, chlorinated phenols, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDFs) (Interagency Task Force on Hazardous Waste 1979; Elder *et al.* 1981; Kuntz and Warry 1983; Jaffe and Hites 1984; NRTC 1984; Gradient Corp./Geotrans Inc. 1988; Monenco 1991; Raven 1991; US EPA and NYSDEC 2002; Williams and O'Shea, 2003).

Since 1980, the Ontario Ministry of Environment (MOE) has undertaken routine and specialized biomonitoring of contaminants in the Niagara River using caged mussels (*Elliptio complanata*) in addition to other long term monitoring programs (spottail shiner contaminant monitoring and the sport fish contaminant monitoring program), as part of Ontario's commitment to the NRTMP. The mussel biomonitoring program has provided information on suspected contaminant sources and source areas and the effectiveness of site remediation in reducing contaminants in the river between Fort Erie and Niagara-on-the-Lake (NOTL) (Kauss 1987; Kauss and Angelow 1988; Anderson *et al.* 1991; Richman 1992-2003).

Biomonitors are an effective means of detecting bioaccumulative contaminants in the water when ambient concentrations are too low to be measured directly using conventional water sampling and analytical methods. The principle behind the mussel biomonitoring program is to take organisms from an uncontaminated site and place them in an environment that is known or suspected of being contaminated with persistent bioaccumulative substances. The biomonitors are left for a specified time to accumulate contaminants and are then analysed to determine the contaminant concentrations in their tissue. By strategically locating the organisms upstream and downstream of a suspected source, the presence or absence of the contaminants in the water body from that source can be determined. The detection of the contaminants in the mussels indicates that these contaminants are bioavailable in the aquatic environment. The absence of a contaminant in the mussel tissue is less definitive. It may suggest that the contaminant is not present or present at such low levels that it does not bioaccumulate to detectable concentrations in the deployed mussels. However, because of the site specific nature of this biomonitor it may also mean that the

mussels were not placed near enough to the source to adequately detect the presence of the contaminants.

The freshwater mussel, *Elliptio complanata*, is a filter feeder feeding on plankton and organic detritus and will, therefore, accumulate contaminants directly from the water column and from particulate matter (Pennak 1978). This method of feeding renders the mussel a good biomonitor since contaminants tend to partition between the dissolved phase and the solid phase where they become associated with sediment or suspended particulates through adsorptive processes. Mussels are abundant and easily collected and transported. They are sedentary organisms and responsive to their environment. Mussels can integrate short term fluctuations in contaminant levels and, accordingly, tissue concentrations reflect short term contaminant pulses which may not be detected by routine water quality monitoring (Muncaster *et al.* 1989; Metcalfe and Charlton 1990; Kauss and Hamdy 1991; Lobel *et al.* 1991). Conversely, because the sampling design is limited to a particular deployment period, results only reflect the exposure during that period. The results obtained at any one sampling event represent the current contamination integrated by that specific organism and cannot be extrapolated to yearly loadings from sources. Likewise, significant contaminant inputs could be missed if they occur outside the designated period of biomonitoring.

Objectives

The general objective of the mussel biomonitoring program is to monitor the distribution of contaminants in the Niagara River and identify areas of concern for point and non-point source investigations.

More specific objectives of this survey were to investigate:

- how tissue contaminant concentrations of caged mussels deployed in the Niagara River for 21 days varied spatially among the stations*
- the qualitative temporal patterns associated with the presence/absence of contaminants (i.e. are specific contaminants consistently detected at specific locations over time?).*
- the effectiveness of remedial actions at point and non-point sources*

This report presents the results of the 2003 mussel biomonitoring survey.

METHODS

Field Sampling and Station Locations

Caged Mussels

The mussels used for the study originated from Balsam Lake (a relatively uncontaminated lake located in Victoria County, Ontario). Mussels of approximately the same size (between 6.5 and 7.2 cm) were collected to reduce variability due to tissue weight and mussel age. The mussels were collected by divers and placed in buckets lined with clean bioassay (food-grade) polyethylene bags partially filled with lake water for transportation. The bags were sealed with air trapped inside and rapid temperature fluctuations were avoided. Three of these mussels were randomly selected and submitted for tissue analysis to determine initial concentrations of contaminants. These mussels are referred to as the Balsam Lake control mussels in this report.

Caged mussels were deployed for 21 days between July 21 and August 11, 2003 at 34 stations on the Canadian and American sides of the river (Figure 1, Appendix A1-A4 for station latitude/longitude and detailed site maps for the Occidental Chemical facility, Bloody Run Creek and the Pettit Flume). Stations were located at the mouth of tributaries, in the Tonawanda Channel, Chippawa Channel and near known industries and hazardous waste sites. The cages were usually within two to three metres from shore because the study was designed to investigate the impact of shore based sources on water quality rather than ambient river conditions. Two new stations were established in the Erie Canal near Holiday Park, upstream and downstream of the Exolon facility. Mussels were also placed in the Niagara River at the mouth of an outfall extending from the 102nd Street landfill which historically discharged contaminants to the river. As well, a new site in the Niagara River downstream of the mouth of Gill Creek was established in a location closer to the mouth than in previous surveys.

At each station at least five mussels were placed in 30 x 45 cm envelope-shaped cages constructed of 1.25 cm galvanized mesh poultry netting. A nylon rope was attached to the cages and then anchored to the river bottom with a cement block. Cages were also anchored to the bottom using pegs or rocks and sometimes attached to a shoreline structure. The mussels were immediately shucked after retrieval, excess water was drained and the soft tissues were weighed (Appendix B), individually wrapped in hexane-rinsed aluminum foil, and placed in plastic bags. Three individual mussels from each station were analysed for percent lipid, organochlorine pesticides (OCs), total PCBs, chlorinated benzenes (CBs), and polycyclic aromatic hydrocarbons (PAHs) (Table 1). The remaining mussels were frozen and archived.

At 11 of these sites an additional four mussels were composited into one sample for dioxin/furan and dioxin-like PCB analysis. Although polybrominated diphenyl ethers (PBDEs) were not identified as a priority contaminant within the NRTMP they have been

Figure 1: Station Locations for the Niagara River
Biomonitoring Survey, 2003



TABLE 1: Mussel tissue and sediment analyses.

"w" represents the smallest amount of an analyte that can be detected, trace values (t) are between "w" and 10 times "w"

All mussel samples were submitted for the following analysis: (ng/g)				Mussels and sediment from selected stations were submitted for:
	w value		w value	
PCBs (total)	20	2,4,5-trichlorotoluene	1	Polychlorinated dibenzo-p-dioxins
Heptachlor	1	2,3,6-trichlorotoluene	1	Polychlorinated dibenzofurans
Aldrin	1	2,6-dichlorobenzyl chloride	1	
Photomirex	5			Polybrominated diphenyl ethers
Mirex	5	Polycyclic aromatic hydrocarbons		
α-BHC	1	Acenaphthene	20	Sediment from a selected number of stations were submitted for:
β-BHC	1	Acenaphthylene	20	Congener specific PCBs
γ-BHC	1	Anthracene	20	
α-chlordane	2	Benzo(a)anthracene	20	
γ-chlordane	2	Benzo(a)pyrene	40	
Oxychlordane	2	Benzo(b)fluoranthene	20	
pp-DDE	1	Benzo(k)fluoranthene	20	
op-DDT	5	Chrysene	20	
pp-DDD	5	Dibenzo(ah)anthracene	40	
pp-DDT	5	Fluoranthene	20	
DDT & metabolites	2	Fluorene	20	
Octachlorostyrene	1	Benzo(g,h,i)perylene	40	
Toxaphene	50	Indeno(1,2,3-cd)pyrene	40	
Hexachloroethane	1	Naphthalene	20	
Hexachlorobutadiene	1	Phenanthrene	20	
1,3,5-trichlorobenzene	2	Pyrene	20	
1,2,4-trichlorobenzene	2			
1,2,3-trichlorobenzene	2			
1,2,4,5-tetrachlorobenzene	1			
1,2,3,4-tetrachlorobenzene	1			
1,2,3,5-tetrachlorobenzene	1			
Pentachlorobenzene	1			
Hexachlorobenzene	1			

identified as a global pollutant. The ministry laboratory recently developed a method to analyse for PBDEs so additional mussels were also deployed to assess bioavailability in the Niagara River and variability in concentrations between mussels deployed within a site. Due to laboratory error during sample processing, mussel data for all of these analyses are only available from a limited number of sites.

Retrieval of caged mussels for the three week survey was successful at all stations with the exception of Bloody Run Creek (station 17) and one station monitoring the 102nd Street Landfill. Mussel cages from these two sites were either vandalized or the cages drifted off site and were not visible. Because of the loss, the 102nd Street site was assessed using the newly established station located at an historical outfall. Since there was no alternative for Bloody Run Creek, mussels were deployed again in 2004. In 1994 a rock slide buried the location of the mouth of the creek so the placement of cages to capture runoff from the site has been problematic. To better define Bloody Run Creek as a source of contamination to the Niagara River four new stations along the shoreline in the vicinity of the Creek, as well as the previously established upstream and downstream stations were monitored (Appendix A3). The mussels were deployed on July 14, 2004 and retrieved on August 4th, 2004. All mussels were successfully retrieved, with the exception of those at one station where the cages were found to be above water. Five additional Balsam Lake mussels were analysed for contaminants as controls during this survey.

Sediment

Surficial sediment samples (top 3 cm) were collected from eight stations for congener specific analysis for PCBs and from 11 stations for the analysis of polychlorinated dibenzop-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs), particle size and TOC. Sediment was collected using a hexane rinsed stainless steel spatula and placed in amber glass jars. Samples were kept on ice in the field, and refrigerated at 4°C in the dark until analysis. The general sediment composition (e.g., sand, silt etc.), sediment colour, and any unusual features were recorded.

Analytical Methods

All laboratory analytical procedures for contaminants in mussels and sediment, and for particle size analysis in sediment, followed the methodology outlined in the Hames Handbook of Analytical Methods for Environmental Samples (OMOE 1983). Procedural updates for biomaterial and sediment analysis are provided in OMOE (2004a-e; 2005 a-c). All results for mussels are reported on a wet weight basis. Results for sediment are reported on a dry weight basis.

Data Analysis

The mussel concentrations of each analyte are provided in tables summarized within the report. A period (.) in a column for organochlorine pesticides, total PCBs, PAHs and chlorinated benzenes indicates that the analyte was not present above the detection limit

denoted by "W". "W" represents the smallest amount of an analyte that can be reliably detected by the procedure used. Concentrations described as "trace" are flagged with a "<T". Trace values ranged from greater than "W" to 10 times "W" for organic parameters. Data flagged as trace indicate that the presence of the analyte is confirmed but the actual concentrations reported should be interpreted with caution. Basically, "T" indicates the limit of quantification. Both "W" and "T" are based on the precision of the method which is in turn based on replicate measurements for the same analyte. "W" is set at 2/3 of the standard deviation of the replicate measurements of low-level spiked blank matrix samples. Each sample run (generally 12 to 25 samples) is compared against a prepared standard and includes the determination of low level detection limits, method blanks and recovery checks using spikes. An independent control standard is used to monitor accuracy and stability, duplicate samples are used to test within run precision and calibration standards are used for a drift check. Details on QA/QC expectations are provided in the method manuals listed above.

In the case of dioxins and furans, dioxin-like PCBs and PBDEs a run usually consisted of 10 samples. An analyte was considered to be above the detection limit when the result met standard peak definition (usually 3-5 times signal:noise ratio) or was greater than five times a corresponding positive result determined to be present in the method blank used within that specific sample set. "W" and "T" values do not apply to these analytical procedures. Data that do not meet peak definition and/or are less than five times the method blank are flagged as "<". Data were also flagged as "<" if there were matrix effects and interferences. For PBDEs, all data were blank subtracted prior to reporting.

All data have been summarized in tables within the report (Tables 1-8). The 2004 study design from Bloody Run Creek had a sufficient number of samples to provide an opportunity to statistically compare concentrations in mussels deployed at the site with concentrations upstream and downstream of the site. Typically, for other stations in the survey where there is insufficient data for statistical analysis, a site is identified as a potential source based on the presence or absence of the contaminant in the mussels (e.g. PCBs at the mouth of Two Mile Creek which is a tributary to the Niagara River), and will be compared with an upstream site where available (e.g. Pettit Flume Cove and site upstream of the cove, Gratwick Riverside Park and site upstream of the park).

RESULTS AND DISCUSSION

Balsam Lake Control Mussels

In 2003, organochlorine pesticides and chlorinated benzenes were not detected in the Balsam Lake control mussels. However, one of the three control mussels measured 42 ng/g total PCB. Mussel data presented in Table 2 were not corrected for this concentration. The contamination of one of the Balsam Lake control mussels suggested that mussels may have had as much as 42 ng/g total PCB prior to deployment, or a more likely explanation

would be that the sample was contaminated at some point during sample processing and/or analysis. However, note that the five additional Balsam Lake control mussels from the 2004 deployment at Bloody Run Creek did not have any detectable concentrations of total PCBs (Table 2a). As well, previous Niagara River mussel monitoring surveys since 1983 have not reported the presence of total PCBs in any Balsam Lake samples. Additionally, the PCB concentrations reported in Table 2 for the Canadian and U.S. sites monitored are consistent with previous years of monitoring.

Dioxin-like PCB analysed in mussels using a different procedure with a lower detection limit than the procedure used for total PCBs, were present in the Balsam Lake mussel sample (composite of four mussels) at low concentrations. The total TEQ concentration in 2004 (0.11 pg/g) was lower than the concentration measured in 2000 (the earliest available data for these compounds) which was 0.57 pg/g. This suggested the presence of some PCB isomers in the Balsam Lake mussels but only at very low concentrations. Concentrations of the dioxin-like PCBs in the Balsam Lake mussels were lower than those detected in mussels deployed in the Niagara River in 2003. The cause of the variation in concentration between surveys (2000 vs 20003) is unknown. There are no known sources of PCBs in the area of Balsam Lake. However, a sewage lagoon discharges to the lake twice a year which may be a possible source. Balsam Lake mussel data for dioxin-like PCBs are compared with samples from other sites in the Niagara River in 2003 and 2004 (Table 6a).

Organochlorine Pesticides

With the exception of p,p'-DDE (metabolite of the pesticide DDT), mussels placed at stations on the Canadian side of the river did not accumulate any detectable organochlorine pesticides (Table 2). The frequency of detecting p,p'-DDE at various stations and the trace concentrations present in the mussel tissue (with one exception, concentrations were all less than 7 ng/g), were consistent with previous years of monitoring (Kauss and Angelow 1988; Anderson *et al.* 1991; Richman 1992-2003). Detectable concentrations (i.e. greater than trace values; 10 ng/g) were present in mussels deployed only in Lyons Creek (mean 17 ng/g, SD (standard deviation) 8.1 ng/g). Trace concentrations had been previously detected at this site in 2000. Although p,p'-DDE was not detected in mussels at NOTL or Fort Erie in 2003, trace concentrations were present at these two sites in the past, and juvenile spottail shiners collected by MOE from 2001 to 2003 from Fort Erie and NOTL had detectable concentrations which ranged from 6 to 19 ng/g and from 10 to 26 ng/g, respectively suggesting that DDE is bioavailable in these areas. Concentrations in spottail shiners collected from the mouth of Frenchman's Creek from 2000 to 2003 ranged from 6 to 24 ng/g (MOE unpublished data). These concentrations were below the IJC wildlife criterion of 200 ng/g for DDT (IJC 1988) and suggest background contamination.

The detection of organochlorine pesticides such as pp'-DDE and the hexachlorocyclohexanes (α -HCH, β -HCH and γ -HCH), in mussels deployed along the American side of the Niagara River has always been sporadic (Richman 1992-2003). In this study, trace concentrations of pp'-DDE were detected in mussels deployed at Holiday

TABLE 2: Concentrations (ng/g wet weight) of organochlorine pesticides and total PCBs in mussels introduced to the Niagara River for three weeks, 2003. An analyte less than or equal to "w" is designated as ".". Trace values "<T" represent concentrations between "w" and 10 time "w"

Station Description	Station Number	Field Number	Retrieval Date	Time	Water Depth (m)	Lipid %	α -BHC ng/g 1<=W	β -BHC ng/g 1<=W	p,p'-DDE ng/g 1<=W	Total PCBs ng/g 20<=W	
Canadian Sites											
Fort Erie at Robertson St.	5	2 203	GL035723	14-Aug-03	1410	0.5	0.53
	5	2 203	GL035724	14-Aug-03	1410	0.5	0.20
	5	2 203	GL035725	14-Aug-03	1410	0.5	0.56
Frenchmans Creek - Durez	5	15 19	GL035727	14-Aug-03	1430	0.5	0.45	.	4	<T	.
	5	15 19	GL035728	14-Aug-03	1430	0.5	0.48	.	4	<T	.
	5	15 19	GL035729	14-Aug-03	1430	0.5	0.51
Chippawa Channel	5	2 51	GL035744	15-Aug-03	900	0.5	1.40
	5	2 51	GL035745	15-Aug-03	900	0.5	1.60
	5	2 51	GL035746	15-Aug-03	900	0.5	0.74	.	7	<T	50 <T
Lyons Creek	5	15 20	GL035731	15-Aug-03	800	0.5	0.72	.	26	.	650 P84
	5	15 20	GL035732	15-Aug-03	800	0.5	0.51	.	12	.	250 P84
	5	15 20	GL035733	15-Aug-03	800	0.5	2.00	.	12	.	280 P84
Niagara-on-the-Lake	11	2 9	GL035751	15-Aug-03	1040	0.5	2.30
	11	2 9	GL035752	15-Aug-03	1040	0.5	0.76
	11	2 9	GL035753	15-Aug-03	1040	0.5	0.96
American Sites											
Buffalo River	5	2 220	GL035719	14-Aug-03	1314	0.5	0.50	.	.	28	<T
	5	2 220	GL035720	14-Aug-03	1314	0.5	0.30	.	.	25	<T
	5	2 220	GL035721	14-Aug-03	1314	0.5	0.62	.	.	34	<T
Tonawanda Channel - upstream of Two Mile Creek	5	2 92	GL035715	14-Aug-03	1150	0.5	0.62
	5	2 92	GL035716	14-Aug-03	1150	0.5	0.43	.	.	26	<T
	5	2 92	GL035717	14-Aug-03	1150	0.5	0.17
Two Mile Creek	5	2 197	GL035705	14-Aug-03	1100	0.5	0.47	.	.	82	<T
	5	2 197	GL035706	14-Aug-03	1100	0.5	1.10	.	.	70	<T
	5	2 197	GL035707	14-Aug-03	1100	0.5	1.40	.	.	64	<T
Holiday Park - upstream Exolon	5	15 33	GL035697	14-Aug-03	945	0.5	1.10	.	.	30	<T
	5	15 33	GL035698	14-Aug-03	945	0.5	1.10	.	.	105	<T
	5	15 33	GL035699	14-Aug-03	945	0.5	1.50	.	.	73	<T
Holiday Park - downstream Exolon	5	15 34	GL035701	14-Aug-03	1025	0.5	1.10	.	.	33	<T
	5	15 34	GL035702	14-Aug-03	1025	0.5	1.10	.	.	27	<T
	5	15 34	GL035703	14-Aug-03	1045	0.5	1.80	.	7	<T	62 <T
Pettit Flume - upstream	5	2 185	GL035681	14-Aug-03	820	0.5	0.51
	5	2 185	GL035682	14-Aug-03	820	0.5	0.82	.	4	<T	.
	5	2 185	GL035683	14-Aug-03	820	0.5	0.95
Pettit Flume - Site B	5	2 186	GL035690	14-Aug-03	845	0.5	1.70	.	5	<T	89 <T
	5	2 186	GL035691	14-Aug-03	845	0.5	0.99	.	4	<T	24 <T
	5	2 186	GL035692	14-Aug-03	845	0.5	0.89	.	.	34	<T
Pettit Flume - downstream	5	2 187	GL035693	14-Aug-03	915	0.5	1.60	.	.	22	<T
	5	2 187	GL035694	14-Aug-03	915	0.5	1.60
	5	2 187	GL035695	14-Aug-03	915	0.5	1.40	.	.	25	<T
Mouth of Sewer - downstream Superior Lubricant	5	2 4	GL035622	12-Aug-03	1715	0.5	0.58	.	.	37	<T
	5	2 4	GL035623	12-Aug-03	1715	0.5	0.47	.	.	37	<T
	5	2 4	GL035624	12-Aug-03	1715	0.5	0.54	.	.	35	<T
Gratwick/Riverside Park - upstream	5	2 31	GL035626	12-Aug-03	1730	1.3	0.67	.	.	62	<T
	5	2 31	GL035627	12-Aug-03	1730	1.3	0.40	.	.	39	<T
Gratwick/Riverside Park	5	2 199	GL035628	12-Aug-03	1800	1.2	0.53	.	.	42	<T
	5	2 199	GL035629	12-Aug-03	1800	1.2	0.78	.	.	39	<T
	5	2 199	GL035630	12-Aug-03	1800	1.2	0.76	.	.	35	<T

Station Description	Station Number			Field Number	Retrieval Date	Time	Water Depth (m)	Lipid %	α -BHC ng/g 1<=W	β -BHC ng/g 1<=W	p,p'-DDE ng/g 1<=W	Total PCBs ng/g 20<=W	
Cayuga Creek	5	15	31	GL035618	12-Aug-03	1400	1	0.48	3	<T	6	<T	<T
	5	15	31	GL035619	12-Aug-03	1400	1	0.42	3	<T	3	<T	<T
102nd Street - upstream	5	2	93	GL035634	12-Aug-03	1830	0.5	0.62				35	<T
	5	2	93	GL035635	12-Aug-03	1835	0.5	0.61				28	<T
	5	2	93	GL035636	12-Aug-03	1835	0.5	0.64				46	<T
102nd Street - outfall	5	6	23	GL035637	12-Aug-03	1835	0.3	0.61				39	<T
	5	5	23	GL035638	12-Aug-03	1835	0.3	0.49				43	<T
	5	5	23	GL035639	12-Aug-03	1835	0.3	0.51				51	<T
Occidental - upstream of storm sewer A	5	2	47	GL035678	13-Aug-03	1230	0.5	1.10				24	<T
	5	2	47	GL035679	13-Aug-03	1230	0.5	1.50				56	<T
	5	2	47	GL035680	13-Aug-03	1230	0.5	0.74				27	<T
Occidental - storm sewer A	5	2	46	GL035675	13-Aug-03	1215	0.5	0.95				56	<T
	5	2	46	GL035676	13-Aug-03	1215	0.5	1.50				52	<T
	5	2	46	GL035677	13-Aug-03	1215	0.5	0.71				29	<T
Occidental - storm sewer B	5	2	94	GL035672	13-Aug-03	1200	0.5	1.30				37	<T
	5	2	94	GL035673	13-Aug-03	1200	0.5	1.30				35	<T
	5	2	94	GL035674	13-Aug-03	1200	0.5	1.20				44	<T
Occidental - between storm sewer B & C	5	2	45	GL035669	13-Aug-03	1141	0.5	0.96				28	<T
	5	2	45	GL035670	13-Aug-03	1141	0.5	1.10				63	<T
	5	2	45	GL035671	13-Aug-03	1141	0.5	0.82				26	<T
Occidental - storm sewer C	5	2	44	GL035666	13-Aug-03	1130	0.5	0.78				29	<T
	5	2	44	GL035667	13-Aug-03	1130	0.5	0.45			2	<T	
	5	2	44	GL035668	13-Aug-03	1130	0.5	0.57				32	<T
Occidental - downstream of storm sewer C	5	2	43	GL035663	13-Aug-03	1046	0.5	0.80				39	<T
	5	2	43	GL035664	13-Aug-03	1046	0.5	0.22			2	<T	
	5	2	43	GL035665	13-Aug-03	1046	0.5	0.61				33	<T
Occidental Sewer 003	5	2	42	GL035649	13-Aug-03	1010	0.5	1.20					
	5	2	42	GL035650	13-Aug-03	1010	0.5	0.50					
	5	2	42	GL035651	13-Aug-03	1010	0.5	0.83					
Occidental - storm sewer S&N area	5	2	40	GL035646	13-Aug-03	1000	0.5	0.74				30	<T
	5	2	40	GL035647	13-Aug-03	1000	0.5	1.40				36	<T
	5	2	40	GL035648	13-Aug-03	1000	0.5	0.82				26	<T
Gill Creek (mouth) - upstream of outfall	5	2	37	GL035612	12-Aug-03	1125	1	0.30				63	<T
	5	2	37	GL035613	12-Aug-03	1125	1	0.44	2	<T	2	<T	<T
Gill Creek (mouth) - downstream of outfall	5	2	37	GL035614	12-Aug-03	1125	1	0.61				41	<T
	5	2	37	GL035615	12-Aug-03	1125	1	0.33			2	<T	<T
	5	2	37	GL035616	12-Aug-03	1125	1	0.70			3	<T	<T
Gill Creek - upstream within the creek	5	15	22	GL035603	12-Aug-03	1000	0.7	0.97	3	<T		45	<T
	5	15	22	GL035605	12-Aug-03	1000	0.7	0.45	2	<T	2	<T	<T
Bloody Run Creek - upstream	11	2	18	GL035643	13-Aug-03	900	0.7	0.34					
	11	2	18	GL035644	13-Aug-03	900	0.7	0.60					
	11	2	18	GL035645	13-Aug-03	900	0.7	0.64					
Bloody Run Creek - downstream	11	2	25	GL035640	13-Aug-03	900	0.5	1.10					
	11	2	25	GL035641	13-Aug-03	900	0.5	1.00				29	<T
	11	2	25	GL035642	13-Aug-03	900	0.5	0.82					
Balsam Lake - control	18	1	1	GL035760	25-Jul-03	1200	0.5	1.10				42	<T
	18	1	1	GL035761	25-Jul-03	1200	0.5	0.70					
	18	1	1	GL035762	25-Jul-03	0	0.5	1.40					

All organochlorinated compounds listed in Table 1 but absent from this table were not detected in any mussels deployed in this survey
NOTL=Niagara-on-the-Lake P40-PCB resembled mixture of Aroclor 1256 and 1260 (apply to all PCB data except Lyons Creek)
Lyons Creek - P84-PCB resembled mixture of Aroclor 1248 and 1254

TABLE 2a: Concentrations (ng/g wet weight) of organochlorine pesticides and Total PCBs in mussels introduced to the Niagara River near Bloody Run Creek for three weeks, 2004. An analyte less than or equal to "w" is designated as "." Trace values "<T" represent concentrations between "w" and 10 time "w"

Station Description	Station Number			Field Number	Retrieval Date	Time	Lipid %	p,p'-DDE ng/g	RMK	Total PCBs ng/g	RMK
								1<=W		20<=W	
Bloody Run Creek - upstream	11	2	18	GL043043	04-Aug-04	7:59	0.36	.	.	38	<T
				GL043044	04-Aug-04	7:59	0.29	2	<T	24	<T
				GL043045	04-Aug-04	7:59	0.51	.	.	29	<T
				GL043046	04-Aug-04	7:59	0.31	.	.	40	<T
				GL043047	04-Aug-04	7:59	0.33	.	.	27	<T
Bloody Run Creek	11	2	132	GL043029	04-Aug-04	7:30	0.51	4	<T	98	<T
				GL043030	04-Aug-04	7:30	0.46	7	<T	72	<T
				GL043031	04-Aug-04	7:30	0.45	4	<T	91	<T
				GL043032	04-Aug-04	7:30	0.32	5	<T	88	<T
				GL043033	04-Aug-04	7:30	0.47	2	<T	57	<T
Bloody Run Creek	11	2	131	GL043022	04-Aug-04	7:00	0.5	6	<T	60	<T
				GL043023	04-Aug-04	7:00	0.26	3	<T	52	<T
				GL043024	04-Aug-04	7:00	0.51	9	<T	50	<T
				GL043025	04-Aug-04	7:00	0.42	3	<T	45	<T
				GL043026	04-Aug-04	7:00	0.38	2	<T	52	<T
Bloody Run Creek	11	2	130	GL043015	04-Aug-04	7:00	0.63	3	<T	56	<T
				GL043016	04-Aug-04	7:00	0.95	.	.	50	<T
				GL043017	04-Aug-04	7:00	0.62	3	<T	51	<T
				GL043018	04-Aug-04	7:00	0.69	4	<T	64	<T
				GL043019	04-Aug-04	7:00	0.43	2	<T	43	<T
Bloody Run Creek - downstream	11	2	25	GL043008	04-Aug-04	6:45	0.44	.	.	20	<=W
				GL043009	04-Aug-04	6:45	0.62	.	.	24	<T
				GL043010	04-Aug-04	6:45	0.72	3	<T	34	<T
				GL043011	04-Aug-04	6:45	0.7	.	.	28	<T
				GL043012	04-Aug-04	6:45	0.49	.	.	27	<T
Balsam Lake - control	18	1	1	GL043001	12-Jul-04	12:00	0.8	.	.	.	
				GL043002	12-Jul-04	12:00	0.4	.	.	.	
				GL043003	12-Jul-04	12:00	1	.	.	.	
				GL043004	12-Jul-04	12:00	0.25	2	<T	.	
				GL043005	12-Jul-04	12:00	0.82	.	.	.	

All organochlorinated compound listed in Table 1 but absent from this table were not detected in any mussels deployed in this survey
P40-PCB resembled mixture of Aroclor 1256 and 1260

Park in the Erie Canal, the Pettit Flume upstream station, within the Pettit Flume cove, sites in front of the Occidental Chemical Company (Buffalo Avenue plant), and at the mouth of Gill Creek. Concentrations were low and only one or two of the three mussels analysed had concentrations above the detection limit (1 ng/g). The mussels deployed along the shoreline in the vicinity of Bloody Run Creek in 2004 also had trace concentrations of p,p'-DDE (Table 2a). Surveys since the 1980's have also detected trace concentrations of p,p'-DDE at other sites such as Two Mile Creek and downstream of Gratwick Riverside Park. The sporadic nature of the data suggests that p,p'-DDE is ubiquitous on both sides of the Niagara River at low concentrations due to the historic use of DDT in the Lake Erie and Niagara River watersheds rather than any new present day sources.

Although tissue concentrations of hexachlorocyclohexanes (HCH) have varied between survey years among the three isomers, they have been consistently detected in mussels deployed at Gill Creek (mouth and/or upstream within the creek) and Cayuga Creek.

In 2003 trace concentrations of α -HCH (2 to 3 ng/g) and β -HCH (2 ng/g) were present in mussels deployed upstream within Gill Creek. In 2000, concentrations of α -HCH were higher and ranged from 16 to 26, ng/g while trace concentrations of β -HCH and γ -HCH were also detected. Changes in bioavailability may be in response to rainfall which could increase runoff resulting in higher concentrations of the compounds in the water column affecting contaminant exposure. Since we do not have water quality data this is just speculation. However, rainfall data for the Niagara area showed that there was only 35.4 mm of rain during the period that the mussels were deployed in 2003 compared with 81.3 mm in 2000 (Environment Canada).

Trace concentrations of α -HCH and β -HCH were also present in mussels deployed in Cayuga Creek which was consistent with data collected in 1995 and 1997 surveys although these compound were not detected in 2000 at this site.

Polychlorinated Biphenyls (PCBs)

The ongoing remediation of historical hazardous waste sites, contaminated sediment, and sewer outfalls has reduced the release of PCBs from non-point sources such that decreases in the bioavailability of PCBs has been reflected in the mussel data at specific sites (e.g., Gill Creek at the mouth and within the creek, 102nd Street Landfill). These remediation projects have likely contributed to an overall reduction of PCB loadings to the Niagara River and from the river to Lake Ontario. However, the data do suggest that PCB exposure is pervasive in the Niagara River and that PCBs will likely be bioavailable in the future, similar to the continued bioavailability of DDT and its metabolites (Tables 2 & 2a).

Total PCB concentrations were below the detection limit (20 ng/g) in mussels deployed at NOTL. As well, sediment collected from the site had low total PCB concentrations (calculated as the sum of 55 congeners - 38 ng/g) (Table 3). One mussel deployed along the Chippawa Channel had trace concentrations of total PCBs (50 ng/g) in 2003 which was consistent with data from 2000 (range: below the detection limit (ND) to 40 ng/g). Sediment

TABLE 3: Concentrations (ng/g dry wt.) of congener specific PCBs in sediment collected from the Niagara River, 2003. Congeners flagged with "<=w" are below the detection limit. "W" values will vary for each congener. Trace values "<T" represent concentrations between "w" and 10 time "w"
(MPC = maximum possible concentration due to chromatographic overlap)

Station Description	Chippawa Channel		Lyons Creek		Niagara-on-the-Lake		Two Mile Creek		Occidental Sewer 003		Gill Creek - upstream of outfall		Gill Creek upstream within creek		Bloody Run Creek	
Station Number	5-2-51		5-15-20		11-2-9		5-2-197		5-2-42		5-2-37		5-15-22		11-2-17	
Field Number	GL035812		GL035811		GL035813		GL035810		GL035805		GL035801		GL035800		GL035803	
Retrieval Date	15-Aug-03		15-Aug-03		15-Aug-03		14-Aug-03		13-Aug-03		12-Aug-03		12-Aug-03		13-Aug-03	
Water Depth (m)	1		0.5		2.5		1		1		1		0.7		0.1	
PCB018	2	<=W	2	<=W	2.3	<T	8.9	<T	280		170		2.9	<T	330	
PCB019	2	<=W	2	<=W	2	<=W	2	<=W	37	<T	3.2	<T	2	<=W	69	
PCB022	0.5	<=W	0.5	<=W	0.5	<=W	0.5	<=W	22		0.7	<T	0.5	<=W	14	
PCB028	1.5	<T	3.3		5.8		20		520		240		9.8		150	
PCB033	1	<T	0.7	<T	1.3	<T	8.7		130		84		1	<T	82	
PCB037	1	<=W	1	<=W	1	<=W	5.1	<T	140		120		3.5	<T	140	
PCB044	0.1	<=W	0.1	<=W	0.6		24		540		230		6.5		620	
PCB049	0.8		9.1		2.9		26		760		300		12		130	
PCB052	1.9		14		1.7		47		1100		410		16		240	
PCB054	2.8		7.6		1.2		3.4		12		45		6.7		150	
PCB070	1.4		8.3		3		26		1100		380		13		490	
PCB074	0.4		2.8		1.3		12		520		170		3.7		220	
PCB077	0.2		0.2		0.2		2.1		11		1.4		0.2		410	
PCB081	0.5	<=W	0.5	<=W	0.5	<=W	0.5	<=W	0.5	<=W	0.5	<=W	0.5	<=W	0.5	<=W
PCB087	0.1	<=W	0.1	<=W	0.1	<=W	0.1	<=W	0.1	<=W	0.1	<=W	0.1	<=W	0.1	<=W
PCB095	0.9		10		5.8		77		1400		550		22		630	
PCB099	0.4		3.4		1		22		300		91		3.9		100	
PCB101	1.2		3.1		0.2		42		400		150		3.5		170	
PCB104	1.7		1.8		2.4		0.9		200		0.1	<=W	1.7		110	
PCB105	0.1	<=W	0.1	<=W	0.1	<=W	2		5.5		1.6		0.1	<=W	83	
PCB110	0.1	<=W	0.1	<=W	0.1	<=W	35		77		53		3.6		170	
PCB114	0.1	<=W	0.1	<=W	0.1	<=W	1		19		5		0.9		33	
PCB118	0.8		3.3		0.3		28		370		130		8.7		230	
PCB119	0.1	<=W	0.1	<=W	0.1	<=W	0.5		7.6		3.7		0.5		80	
PCB123	0.2	<=W	0.2	<=W	0.2	<=W	0.8	MPC	48	MPC	14	MPC	1	MPC	150	MPC
PCB126	0.1	<=W	0.1	<=W	0.1	<=W	0.3		140		1.9		0.1	<=W	730	
PCB128	0.2	<=W	0.2	<=W	0.2	<=W	0.2	<=W	0.2	<=W	0.2	<=W	0.2	<=W	26	
PCB138	0.2	<=W	1.8		0.6		47		100		44		5.9		62	
PCB149	0.7		2.5		1		41		44		39		1.4		150	
PCB151	0.1	<=W	0.8		0.4		8		37		7.6		0.4		110	
PCB153	0.8		1.6		1.3		36		59		30		4.3		140	
PCB155	0.2		0.6		0.1	<=W	1.5		7.5		15		0.1	<=W	12	
PCB156	0.2	<=W	0.2	<=W	0.2	<=W	2.7		2.6		4.8		0.2	<=W	190	
PCB157	0.2	<=W	1		0.4		12		2.6		3.2		0.8		28	
PCB158	0.1	<=W	0.1	<=W	0.1	<=W	3.8		18		4.4		0.6		45	
PCB167	0.2	<=W	0.2	<=W	0.2	<=W	0.6		5.8		0.4		0.4		49	
PCB168	0.1	<=W	2.5	MPC	0.1	<=W	11	MPC	57	MPC	10	MPC	2.5	MPC	100	MPC
PCB169	0.1	<=W	1.1		0.1	<=W	9.2		11		0.8		1.3		150	
PCB170	0.2	<=W	0.8		0.4		13		9		3.7		2		50	
PCB171	0.2	<=W	0.3	<T	0.5		9.3		11		0.8		0.3	<T	380	
PCB177	0.1	<=W	0.1	<=W	0.4		4.4		4.3		0.2		0.2		69	

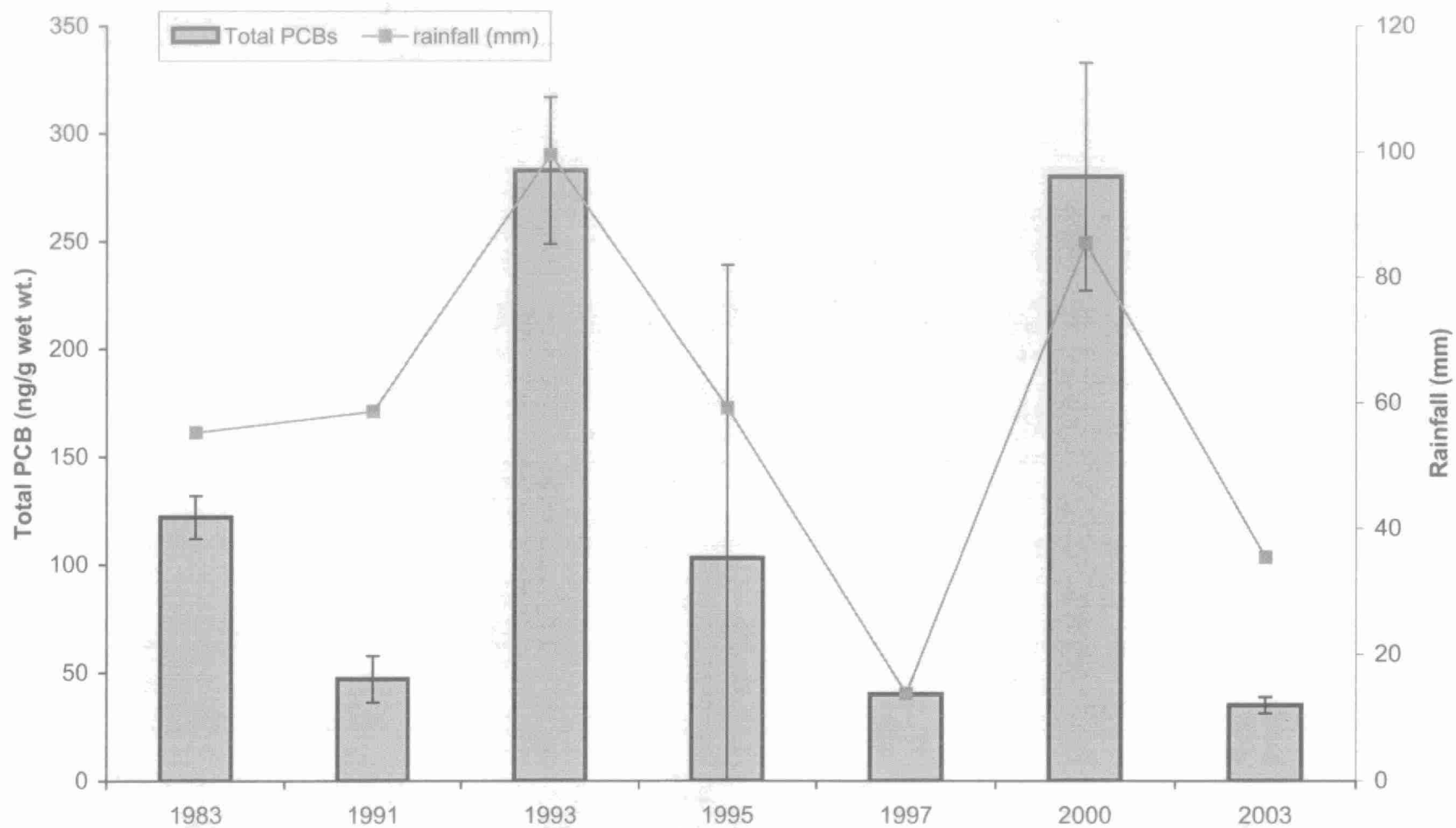
Station Description	Chippawa Channel		Lyons Creek		Niagara-on-the-Lake		Two Mile Creek		Occidental Sewer 003		Gill Creek - upstream of outfall		Gill Creek upstream within creek		Bloody Run Creek
Station Number	5-2-51		5-15-20		11-2-9		5-2-197		5-2-42		5-2-37		5-15-22		11-2-17
PCB178	0.2	<=W	0.2	<=W	0.2	<=W	37		95		36		0.2	<=W	93
PCB180	0.5		1.6		0.9		21		23		5.7		3		38
PCB183	0.2	<=W	0.6		0.3	<T	5.1		8.7		1.3		0.9		27
PCB187	0.4		1		0.5		10		14		2.9		0.3		70
PCB188	0.1	<=W	0.1	<=W	0.1	<=W	5		13		4.5		1.3		87
PCB189	0.2	<=W	0.2	<=W	0.2	<=W	0.8		4.2		15		0.4		33
PCB191	0.2	<=W	0.2	<=W	0.2	<=W	0.4		3.1		0.4		0.2	<=W	14
PCB194	0.2	<=W	0.5		0.2	<=W	4.1		6.3		1.5		0.9		25
PCB199	0.2	<=W	0.6		0.5		4.8		5.7		0.4		0.5		210
PCB201	0.2	<=W	0.2	<=W	0.2	<=W	11		21		3.3		0.2	<=W	82
PCB202	0.2	<=W	0.2	<=W	0.2	<=W	0.8		40		0.2	<=W	0.2	<=W	93
PCB205	0.2	<=W	0.2	<=W	0.2	<=W	0.2	<=W	0.2	<=W	0.2	<=W	0.2	<=W	2
PCB206	0.3	<T	0.4		0.4		2		2.3		1.5		0.5		3.4
PCB208	0.3	<T	0.4		0.4		1		13		0.8		0.6		12
Total PCB (ng/g)	19		87		38		690		8800		3400		150		7900
Total PCB normalized for TOC	2714		3107		5429		10615		1100000		485714		8824		359091
TOC (mg/g)	7		28		7		65		8		7		17		22
Clay (%)	7		25		6		19		7		32		16		14
Silt (%)	24		62		19		63		19		54		61		55
Sand (%)	69		13		75		18		58		14		23		31

collected from this site in 2003 also had low concentrations of PCB (19 ng/g). The highest PCB concentrations detected in the 2003 survey were present in mussels deployed in Lyons Creek (range: 250 to 650 ng/g) which is a site in Ontario known to be contaminated with PCBs. The PCBs in the mussels resembled a mixture of Aroclor 1248 and 1254. Previous MOE data showed high sediment concentrations of PCBs (Fletcher and Petro, 2005), however, sediment collected during this survey had relatively low concentrations (87 ng/g). This is likely due to the patchy distribution of the contaminated sediment in the creek. In contrast with the mussel data the PCBs in sediment resembled a mixture of Aroclor 1254 and 1260. Remedial actions to clean up contaminated sediment in Lyons Creek are presently being investigated and are pending the completion of an environmental risk assessment.

Similar to data reported from the 1997 and 2000 surveys, trace concentrations of total PCBs were present in mussels deployed at almost all stations on the American side of the river (Table 2). Generally, concentrations at all stations were similar (with high within site variability at times), making it impossible to identify point or non-point sources.

The highest concentrations of total PCBs for the three week survey in 2000 were present in mussels deployed about 15 m downstream of a sewer associated with the Occidental chemical plant (station 43; Appendix A2-Figure). Concentrations at that site ranged from 240 to 340 ng/g (Richman, 2003). The sewer (station 44) upstream of this site was supposed to be inactive and the mean PCB concentration in mussels at that site was only 53 ng/g (SD 11.5 ng/g), suggesting it was not the source of the higher concentrations downstream of the outfall. As such, the PCBs detected at station 43 may have been due to surface runoff or contaminants leaching through shoreline rock and rubble from contaminated soil. However, in 2003, high concentrations of total PCBs at station 43 were not detected. Total PCB concentrations at both station 43 and 44 were similar to all the other sites associated with the Occidental facility and fell well within the range detected in mussels deployed upstream and downstream along the Niagara River. Station 43 has been monitored since 1983 generating data with high and low concentrations. The only conclusions that can be inferred from this data-set (particularly since there has not been any recent remedial actions to account for the decrease in concentrations), is that the release of PCBs from the site is episodic and may be associated with rainfall and surface runoff as previously suggested. Without actual water quality data this remains as speculation but a review of all rainfall data for the periods of mussel deployment showed that for years when concentrations of total PCBs were high in mussels at this site, rainfall was also consistently high (Figure 2). PCBs have been associated with the Occidental facility since mussel monitoring began in the 1980s, with earlier studies detecting high concentrations in mussels deployed at Sewer 003 (Anderson *et al.* 1991). Since 1991 concentrations have been low or below the detection limit at Sewer 003; however, sediment collected from the mouth of the outfall in 2003 had high total PCB concentrations (8,800 ng/g). Current releases of PCBs to the water column from the outfall (during the period of monitoring) would have been detected in the mussels suggesting that the sediment contamination could possibly be historic and representative of the mussel data collected in the 1980s.

Figure 2: Total PCBs (mean \pm SD) in Caged Mussels Deployed at Station 43 in the Vicinity of the Occidental Chemical Company, Niagara River (1983-2003) and Cumulative Rainfall Data (mm) for the Period of Deployment



Concentrations of total PCBs in Two Mile Creek were similar in 2003 (mean 72 ng/g, SD 9.2 ng/g) to concentrations reported in 1997 and 2000 (mean 93 ng/g, SD 11.5 ng/g in both surveys) and have not changed significantly since earlier surveys (Figure 3). PCBs have been detected in mussels deployed in Two Mile Creek in surveys dating back to 1987. This creek has been identified by NYSDEC as being contaminated with PCBs due to ongoing active sources (e.g. storm sewers located upstream) (Niagara River Secretariat 2002). NYSDEC is currently investigating sources of PCBs to the creek and possible remedial actions. Sediment collected from the creek in 2003 had a total PCB concentration of 690 ng/g.

Total PCB concentrations in mussels deployed at the mouth of Gill Creek have been consistently low in recent surveys when compared with concentrations detected in mussels prior to the remediation of the site (Figure 4). A major clean up of PCB contaminated sediment in Gill Creek upstream of the mouth was completed in 1992. Gill Creek was historically a known PCB "hot spot" (Interagency Task Force on Hazardous Waste 1979; Raven 1991), and a significant source of PCBs to the Niagara River and subsequently Lake Ontario. Concentrations in 2003 (mean and standard deviation of the two stations located downstream of the Creek mouth; 59 ng/g, SD 9.7 ng/g) were similar to 2000. PCBs were present in sediment collected from the mouth of the creek possibly reflecting historic contamination (3,400 ng/g).

Another site in Gill Creek, north of Highway 384 (upstream of the area previously remediated for PCBs), typically had high concentrations of PCBs in mussels and juvenile fish suggesting additional source(s) of PCBs to this area (Preddice *et al.* 2002; Richman 1993; Richman 1997). Contamination of this site was confirmed by NYSDEC and remedial actions in the area to remove contaminated sediment were completed in 1998. Sediment PCB concentrations in 2003 were low (150 ng/g). Total PCBs were detected in mussels deployed at this site in 2000, however, concentrations were similar to levels detected at most sites in the Niagara River (mean 80 ng/g). In 2003 concentrations were lower than in 2000 with a mean concentration of 38 ng/g (SD 9.9 ng/g). Prior to site remediation the mean concentration in mussels in 1993 was 157 ng/g (SD 27.7 ng/g) and in 1995 was 200 ng/g (SD 138.5 ng/g) (Richman 1994, 1997).

The 2004 PCB data from Bloody Run Creek suggested that the site is a source of PCBs to the river. Mean concentrations in mussels deployed upstream (31.6 ng/g, SD 7.02 ng/g) and downstream (26.6 ng/g, SD 5.18 ng/g) of the site were similar to results from 2003 and similar to concentrations reported for other sites in the Niagara River (Table 2 & Table 2a; Appendix A3 - Figure). However, a one way analysis of variance (ANOVA) and Tukey pairwise test for multiple comparisons (Appendix C) showed that mean PCB concentrations in mussels deployed at the three stations along the shoreline where Bloody Run Creek discharges to the river (62 ng/g SD 17.4 ng/g) were significantly higher than the upstream or downstream sites ($F = 26.5$, $p < 0.001$) (Figure 5). Sediment collected from the area had high total PCB concentrations (7,900 ng/g) indicating that the sediment is contaminated. Total PCBs in both sediment and mussels resembled a mixture of Aroclor 1254 and 1260.

Figure 3: Total PCBs (mean \pm SD) in Caged Mussels Deployed in Two Mile Creek, Niagara River (1987-2003)

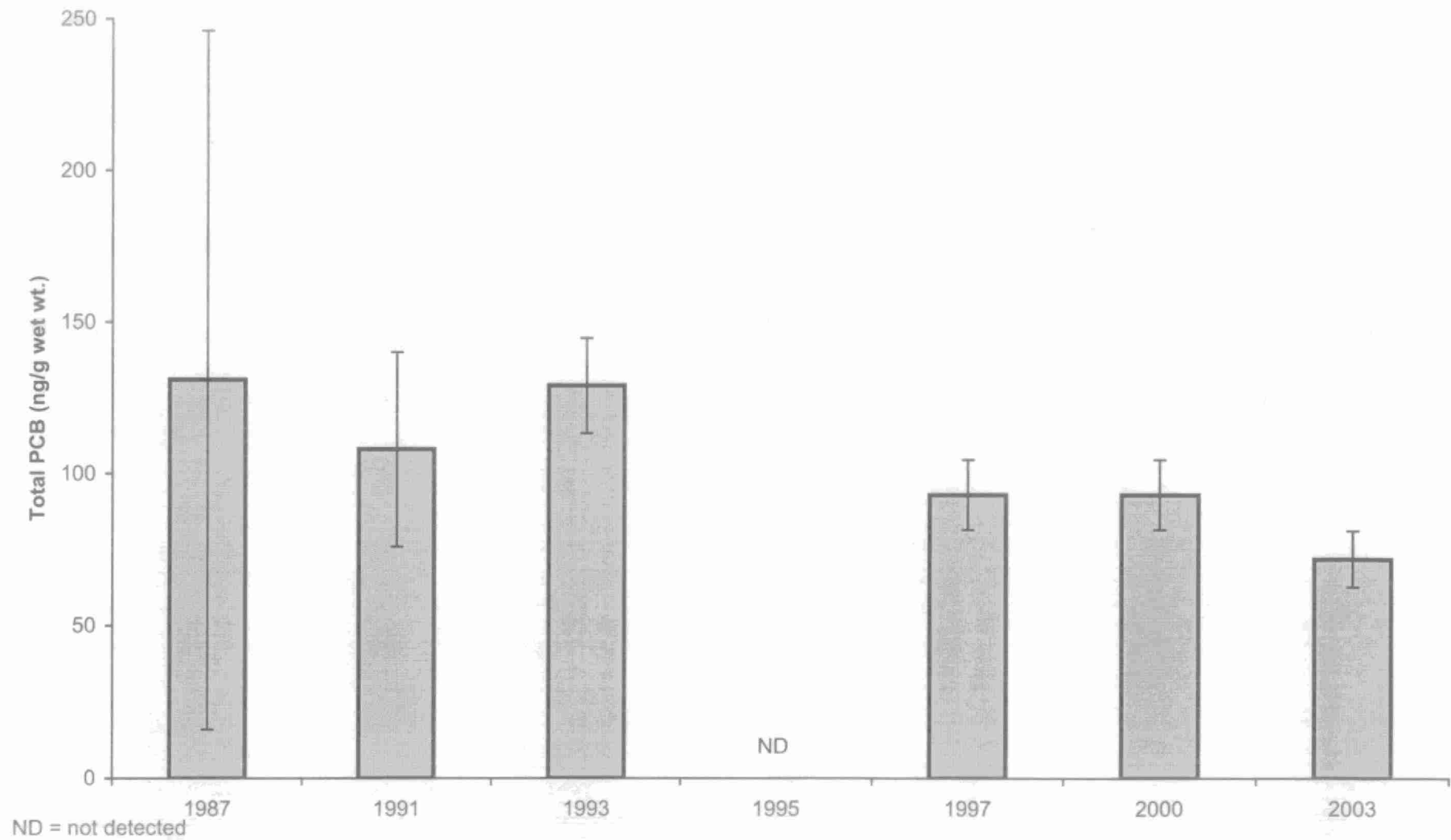


Figure 4: Total PCBs (mean \pm SD) in Caged Mussels Deployed at the Mouth of Gill Creek (1983-2003)

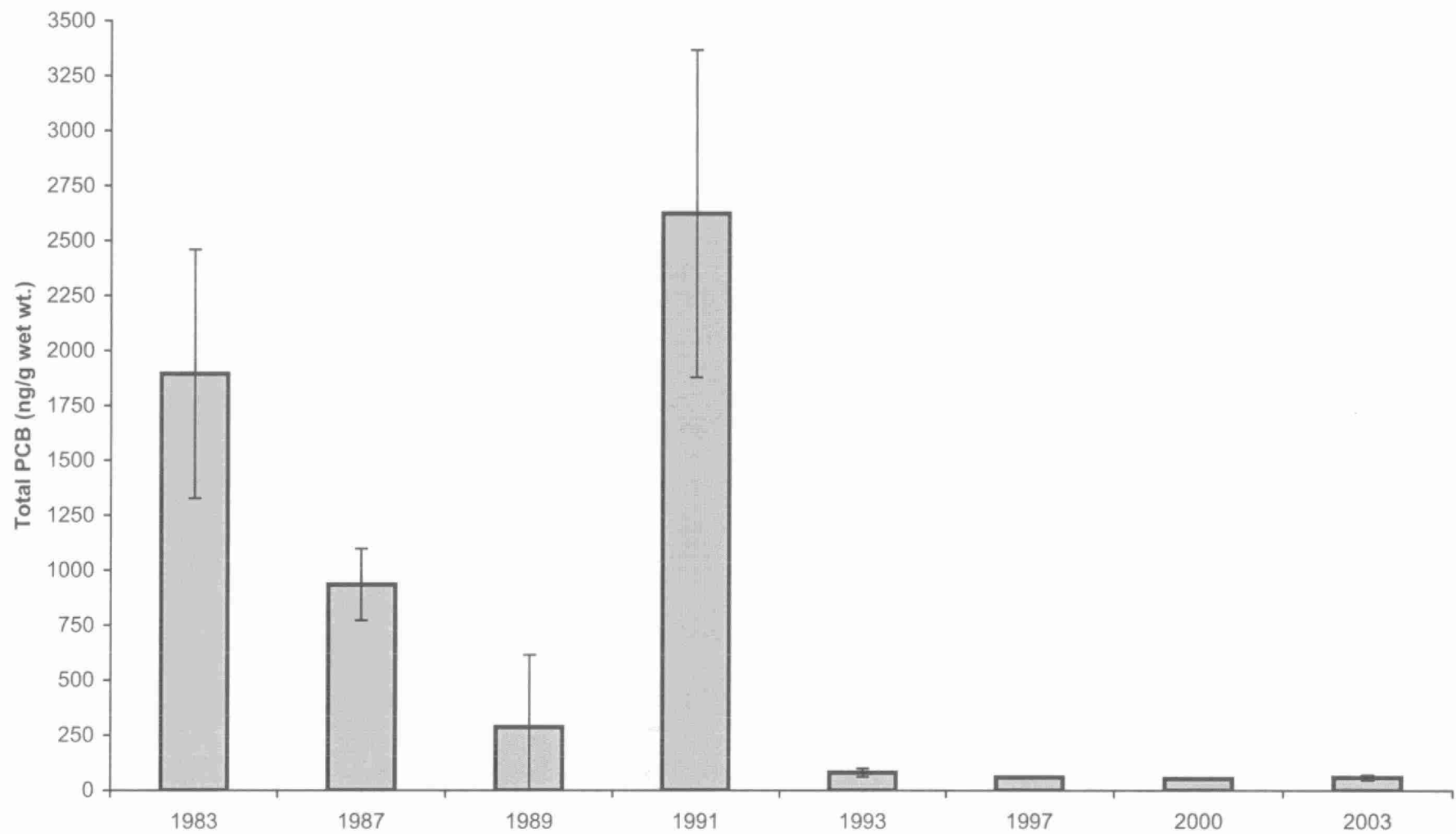
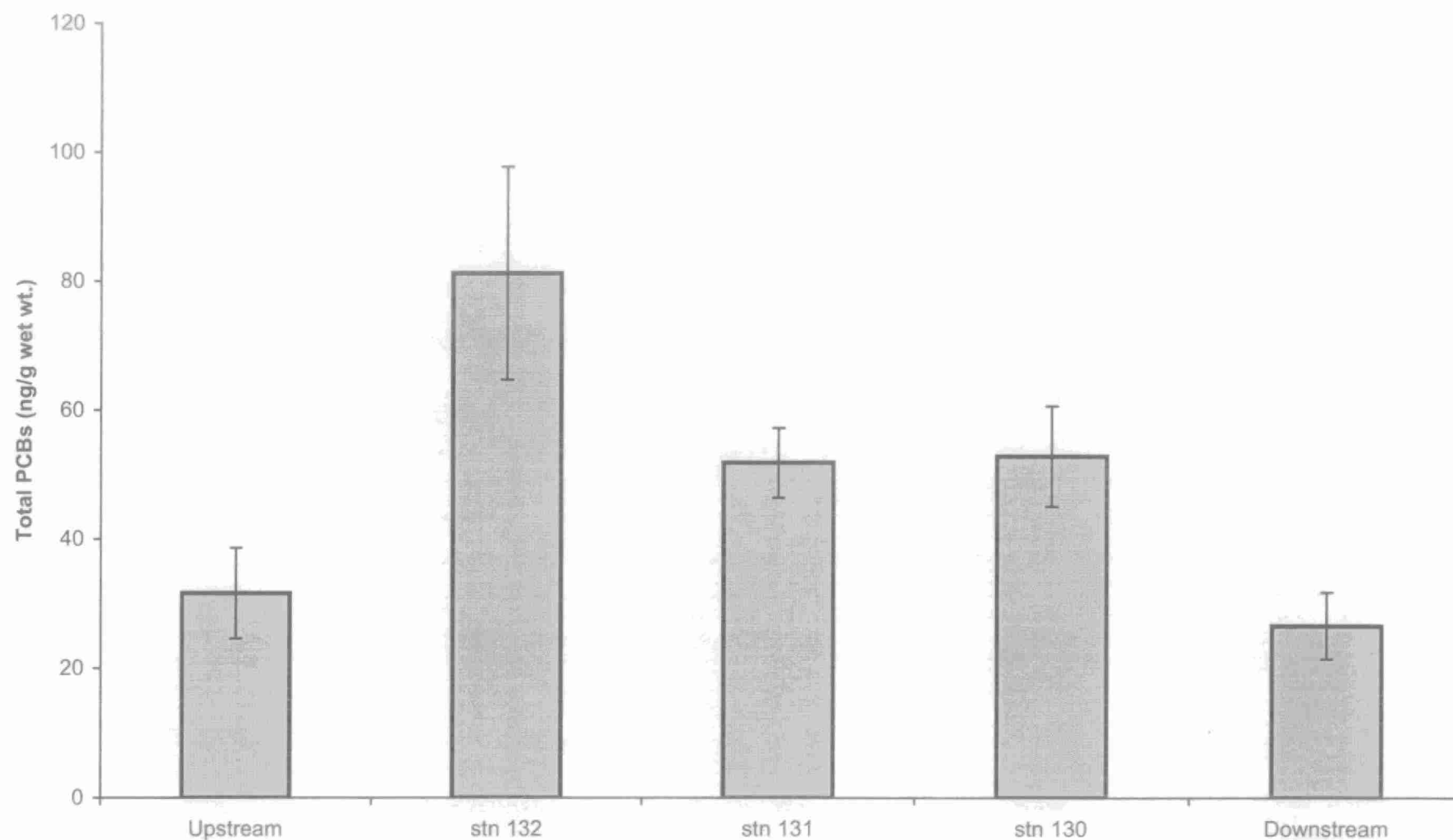


Figure 5: Total PCBs (mean \pm SD) in Caged Mussels Deployed Along the Shoreline of the Niagara River Near the Mouth of Bloody Run Creek, 2004



The available data does not permit the identification of the source of PCBs to the mussels i.e. whether it is the resuspension of PCB contaminated sediment and subsequent accumulation of particulate matter by the mussels or whether PCBs are available in the seepage water flowing into the Niagara River.

Chlorinated Benzenes and Industrial Compounds

Chlorinated benzenes were not detected in any mussels deployed on the Canadian side of the river which is consistent with past surveys.

The most frequently detected chlorinated compounds on the American side of the river in mussel tissue were hexachlorobutadiene (HCBd), 1,2,3,5-tetrachlorobenzene and 2,3,6-trichlorotoluene (Table 4 & 4a). Hexachlorobenzene (HCB) was identified at most sites but only at trace concentrations. Previous surveys have also had a high frequency of detecting pentachlorobenzene, although in 2003 this did not occur. However, the 2004 survey of Bloody Run Creek found high concentrations of pentachlorobenzene associated with that site (Table 4a). Trichlorobenzenes and octachlorostyrene were not detected at all in 2003, but have been detected sporadically in previous surveys typically at trace concentrations. Although not consistently present in each replicate mussel, 2,3,6- and/or 2,4,5-, and α ,2,6-trichlorotoluene were detected in mussel tissue at several stations; Two Mile Creek, Pettit Flume, Gratwick Riverside Park (upstream and downstream), upstream and downstream of 102nd Street Landfill, and Gill Creek. With the exception of trace concentrations present in the Pettit Flume and 102nd Street Landfill, these compounds had not been present at these sites in previous surveys. The results were confirmed with laboratory analysts. The reason for their occurrence in mussels is unclear at the present time. Perhaps there was an episodic release of these contaminants to the Tonawanda Channel during mussel deployment. Further monitoring will be required to see if they continue to be detected.

In general, chlorinated benzenes were detected at most of the sampling sites associated with the Occidental Chemical Company facility on Buffalo Avenue. Chlorinated benzenes were historically released from the various sewers along the waterfront (NRTC 1984). However, with the exception of 1,2,3,5-tetrachlorobenzene, concentrations in 2003 were all at trace levels. The highest concentrations of 1,2,3,5-tetrachlorobenzene were consistently present in all mussels deployed at stations 47, 46 and 94 (upstream of sewer A, storm sewer A and storm sewer B - Appendix A2-Figure). This compound was detected at sites further downstream along the Occidental property but only at trace concentrations. 2,3,6-trichlorotoluene was also detected in mussels deployed at stations 47, 46 and 94. This pattern of contamination was in contrast to previous surveys where mussels deployed downstream of station 94 typically had higher concentrations of contaminants than the upstream stations along this stretch of the river. In fact, these two compounds were not detected at these three stations in earlier surveys although they have been present in mussels deployed at the other stations associated with the Occidental facility further downstream (Richman 1992-2003). Since the sewers (labelled A and B - Figure A2) are inactive, the source of the contaminants is presently unknown. Possible causes may be runoff from the surrounding area or due to an unknown source upstream of Occidental.

Table 4: Concentrations (ng/g wet wt.) of chlorobenzenes and chlorinated industrial compounds in caged mussels, Niagara River, 2003. An analyte <=W is designated as "." Trace values "<T" are concentrations between "w" and 10 times "w"

Station Description	Station Number			Field Number	Hexa-chlorobutadiene ng/g (wet wt.) 1<=W	REM	Hexa-chlorobenzene ng/g (wet wt.) 1<=W	REM	Penta-chlorobenzene ng/g (wet wt.) 1<=W	REM	1234-Tetrachlorobenzene ng/g (wet wt.) 1<=W	REM	1245-Tetrachlorobenzene ng/g (wet wt.) 1<=W	REM
Canadian Sites														
Fort Erie at Robertson St.	5	2	203	GL035723										
	5	2	203	GL035724										
	5	2	203	GL035725										
Frenchmans Creek - Duréz	5	15	19	GL035727										
	5	15	19	GL035728										
	5	15	19	GL035729										
Chippewa Channel	5	2	51	GL035744										
	5	2	51	GL035745										
	5	2	51	GL035746										
Lyons Creek	5	15	20	GL035731										
	5	15	20	GL035732										
	5	15	20	GL035733										
Niagara-on-the-Lake	11	2	9	GL035751										
	11	2	9	GL035752										
	11	2	9	GL035753										
American Sites														
Buffalo River	5	2	220	GL035719										
	5	2	220	GL035720										
	5	2	220	GL035721										
Tonawanda Channel - upstream of Two Mile Creek	5	2	92	GL035715										
	5	2	92	GL035716										
	5	2	92	GL035717										
Two Mile Creek	5	2	197	GL035705										
	5	2	197	GL035706										
	5	2	197	GL035707					7	<T				
Holiday Park - upstream Exolon	5	15	33	GL035697										
	5	15	33	GL035698							2	<T		
	5	15	33	GL035699										
Holiday Park - downstream Exolon	5	15	34	GL035701										
	5	15	34	GL035702										
	5	15	34	GL035703										
Pettit Flume - upstream	5	2	185	GL035681	5	<T								
	5	2	185	GL035682	7	<T							3	<T
	5	2	185	GL035683									3	<T
Pettit Flume - Site B	5	2	186	GL035690							2	<T		
	5	2	186	GL035691							10			
	5	2	186	GL035692							7	<T		
Pettit Flume - downstream	5	2	187	GL035693										
	5	2	187	GL035694									7	<T
	5	2	187	GL035695										
Mouth of Sewer - downstream Superior Lubricant	5	2	4	GL035622					2	<T	2	<T		
	5	2	4	GL035623										
	5	2	4	GL035624										
Gratwick/Riverside Park - upstream	5	2	31	GL035626			3	<T	2	<T	7	<T		
	5	2	31	GL035627			2	<T						
Gratwick/Riverside Park	5	2	199	GL035628			2	<T						
	5	2	199	GL035629	16								21	
	5	2	199	GL035630										
Cayuga Creek	5	15	31	GL035618			2	<T						
	5	15	31	GL035619										

Table 4: Concentrations (ng/g wet wt.) of chlorobenzenes and chlorinated industrial compounds in caged mussels, Niagara River, 2003. An analyte <=W is designated as "." Trace values "<T" are concentrations between "w" and 10 times "w"

Station Description	Station Number			Field Number	Hexa-chlorobutadiene ng/g (wet wt.)	REM	Hexa-chlorobenzene ng/g (wet wt.)	REM	Penta-chlorobenzene ng/g (wet wt.)	REM	1234-Tetrachlorobenzene ng/g (wet wt.)	REM	1245-Tetrachlorobenzene ng/g (wet wt.)	REM
102nd Street - upstream	5	2	93	GL035634	.		2	<T	.		.		.	
	5	2	93	GL035635	
	5	2	93	GL035636	.		2	<T	.		.		.	
102nd Street - outfall	5	5	23	GL035637	.		2	<T	.		.		.	
	5	5	23	GL035638	
	5	5	23	GL035639	.		2	<T	.		.		.	
Occidental - upstream of storm sewer A	5	2	47	GL035678	
	5	2	47	GL035679	.		.		.		3	<T	.	
	5	2	47	GL035680	4	<T	
Occidental - storm sewer A	5	2	46	GL035675	.		.		.		2	<T	.	
	5	2	46	GL035676	.		.		.		2	<T	.	
	5	2	46	GL035677	.		2	<T	.		2	<T	.	
Occidental - storm sewer B	5	2	94	GL035672	
	5	2	94	GL035673	.		.		3	<T	3	<T	.	
	5	2	94	GL035674	.		2	<T	.		.		.	
Occidental - between storm sewer B & C	5	2	45	GL035669	12		.		.		.		7	<T
	5	2	45	GL035670	
	5	2	45	GL035671		4	<T
Occidental - storm sewer C	5	2	44	GL035666		3	<T
	5	2	44	GL035667		5	<T
	5	2	44	GL035668	4	<T	.		.		.		3	<T
Occidental - downstream of storm sewer C	5	2	43	GL035663	13		2	<T	.		.		7	<T
	5	2	43	GL035664	3	<T	2	<T	.		.		.	
	5	2	43	GL035665	6	<T	2	<T	.		.		.	
Occidental Sewer 003	5	2	42	GL035649	32		7	<T	6	<T	4	<T	5	<T
	5	2	42	GL035650	29		8	<T	12		4	<T	7	<T
	5	2	42	GL035651	21		5	<T	7	<T	3	<T	3	<T
Occidental - storm sewer S&N area	5	2	40	GL035646	.		2	<T	.		.		.	
	5	2	40	GL035647	8	<T	3	<T	.		.		6	<T
	5	2	40	GL035648	.		2	<T	.		.		.	
Gill Creek (mouth) - upstream of outfall	5	2	37	GL035612	35		3	<T	.		.		17	
	5	2	37	GL035613	37		4	<T	.		.		23	
Gill Creek (mouth) - downstream of outfall	5	2	37	GL035614	13		.		.		.		12	
	5	2	37	GL035615	15		.		.		.		18	
	5	2	37	GL035616	20		2	<T	.		.		12	
Gill Creek - upstream within the creek	5	15	22	GL035603	.		2	<T	.		3	<T	.	
	5	15	22	GL035605		13	
Bloody Run Creek - upstream	11	2	18	GL035643	4	<T	2	<T	.		.		5	<T
	11	2	18	GL035644	
	11	2	18	GL035645	6	<T	3	<T	.		.		3	<T
Bloody Run Creek - downstream	11	2	25	GL035640	6	<T	7	<T	3	<T	.		.	
	11	2	25	GL035641	.		9	<T	.		9	<T	.	
	11	2	25	GL035642	10		6	<T	.		.		.	
Balsam Lake - control	18	1	1	GL035760	
	18	1	1	GL035761	
	18	1	1	GL035762	

Table 4: Concentrations (ng/g wet wt.) of chlorobenzenes and chlorinated industrial compounds in caged mussels, Niagara River, 2003. An analyte <=W is designated as ". " Trace values "<T" are concentrations between "w" and 10 times "w"

Station Description	Station Number		1235- Tetrachlorobenzene ng/g (wet wt.) 1<=W	REM	Hexa- chloroethane ng/g (wet wt.) 1<=W	REM	236- trichlorotoluene ng/g (wet wt.) 1<=W	REM	245- trichlorotoluene ng/g (wet wt.) 1<=W	REM	26A- trichlorotoluene ng/g (wet wt.) 1<=W	REM
Canadian Sites												
Fort Erie at Robertson St.	5	2	203
	5	2	203
	5	2	203
Frenchmans Creek - Durez	5	15	19
	5	15	19
	5	15	19
Chippawa Channel	5	2	51
	5	2	51
	5	2	51
Lyons Creek	5	15	20
	5	15	20
	5	15	20
Niagara-on-the-Lake	11	2	9
	11	2	9
	11	2	9
American Sites												
Buffalo River	5	2	220
	5	2	220
	5	2	220
Tonawanda Channel - upstream of Two Mile Creek	5	2	92
	5	2	92
	5	2	92
Two Mile Creek	5	2	197	13	.	.	6	<T	.	.	4	<T
	5	2	197	11	3	<T
	5	2	197	.	.	.	36	.	25	.	.	.
Holiday Park - upstream Exolon	5	15	33	11	.	.	2	<T	.	.	3	<T
	5	15	33	12	.	.	2	<T	.	.	3	<T
	5	15	33	13	.	.	5	<T	.	.	4	<T
Holiday Park - downstream Exolon	5	15	34	12	4	<T
	5	15	34	11	3	<T
	5	15	34	11	3	<T
Petit Flume - upstream	5	2	185	3	<T	
	5	2	185	4	<T	
	5	2	185	
Petit Flume - Site B	5	2	186	17	.	.	8	<T	.	.	.	
	5	2	186	6	<T	.	31	.	15	.	.	
	5	2	186	16	4	<T
Petit Flume - downstream	5	2	187	13	.	.	35	.	18	.	.	
	5	2	187	.	2	<T	60	.	31	.	.	
	5	2	187	.	.	.	32	.	17	.	.	
Mouth of Sewer - downstream Superior Lubricant	5	2	4	.	.	.	3	<T	.	.	.	
	5	2	4	
	5	2	4	
Gratwick/Riverside Park - upstream	5	2	31	.	.	.	15	.	50	.	.	
	5	2	31	.	.	.	5	<T	8	<T	.	
Gratwick/Riverside Park	5	2	199	3	<T	.	9	<T	22	.	.	
	5	2	199	.	.	.	42	.	12	.	.	
	5	2	199	.	.	.	5	<T	.	.	.	
Cayuga Creek	5	15	31	
	5	15	31	7	<T	.	

Table 4: Concentrations (ng/g wet wt.) of chlorobenzenes and chlorinated industrial compounds in caged mussels, Niagara River, 2003. An analyte <=W is designated as "." Trace values "<T" are concentrations between "w" and 10 times "w"

Station Description	Station Number			1235- Tetrachlorobenzene ng/g (wet wt.)	REM	Hexa- chloroethane ng/g (wet wt.)	REM	236- trichlorotoluene ng/g (wet wt.)	REM	245- trichlorotoluene ng/g (wet wt.)	REM	26A- trichlorotoluene ng/g (wet wt.)	REM
102nd Street - upstream	5	2	93	
	5	2	93	.		.		.		12		.	
	5	2	93	.		.		.		6	<T	.	
102nd Street - outfall	5	5	23	.		.		5	<T	11		.	
	5	5	23	
	5	5	23	
Occidental - upstream of storm sewer A	5	2	47	14		.		39		7	<T	.	
	5	2	47	16		.		9	<T	.		4	<T
	5	2	47	3	<T	.		1	<=W	.		.	
Occidental - storm sewer A	5	2	46	16		.		12		.		4	<T
	5	2	46	16		.		13		.		4	<T
	5	2	46	12		.		2	<T	.		3	<T
Occidental - storm sewer B	5	2	94	14		.		5	<T	.		.	
	5	2	94	11		
	5	2	94	11		
Occidental - between storm sewer B & C	5	2	45	3	<T	
	5	2	45	
	5	2	45	2	<T	.		49		24		.	
Occidental - storm sewer C	5	2	44	
	5	2	44	
	5	2	44	2	<T	
Occidental - downstream of storm sewer C	5	2	43	4	<T	
	5	2	43	
	5	2	43	3	<T	
Occidental Sewer 003	5	2	42	4	<T	
	5	2	42	5	<T	
	5	2	42	4	<T	
Occidental - storm sewer S&N area	5	2	40	
	5	2	40	2	<T	
	5	2	40	
Gill Creek (mouth) - upstream of outfall	5	2	37	.		.		38		28		.	
	5	2	37	.		.		53		16		.	
Gill Creek (mouth) - downstream of outfall	5	2	37	.		.		22		12		.	
	5	2	37	.		.		28		19		.	
	5	2	37	.		.		23		14		.	
Gill Creek - upstream within the creek	5	15	22	2	<T	.		.		4	<T	.	
	5	15	22	.		.		22		14		.	
Bloody Run Creek - upstream	11	2	18	2	<T	
	11	2	18	
	11	2	18	4	<T	
Bloody Run Creek - downstream	11	2	25	
	11	2	25	
	11	2	25	
Balsam Lake - control	18	1	1	
	18	1	1	
	18	1	1	

TABLE 4a: Concentrations (ng/g wet weight) of chlorinated benzenes and chlorinated industrial compounds in mussels introduced to the Niagara River near Bloody Run Creek for three weeks, 2004. An analyte less than or equal to "w" is designated as "w". Trace values "<T" represent concentrations between "w" and 10 time "w".

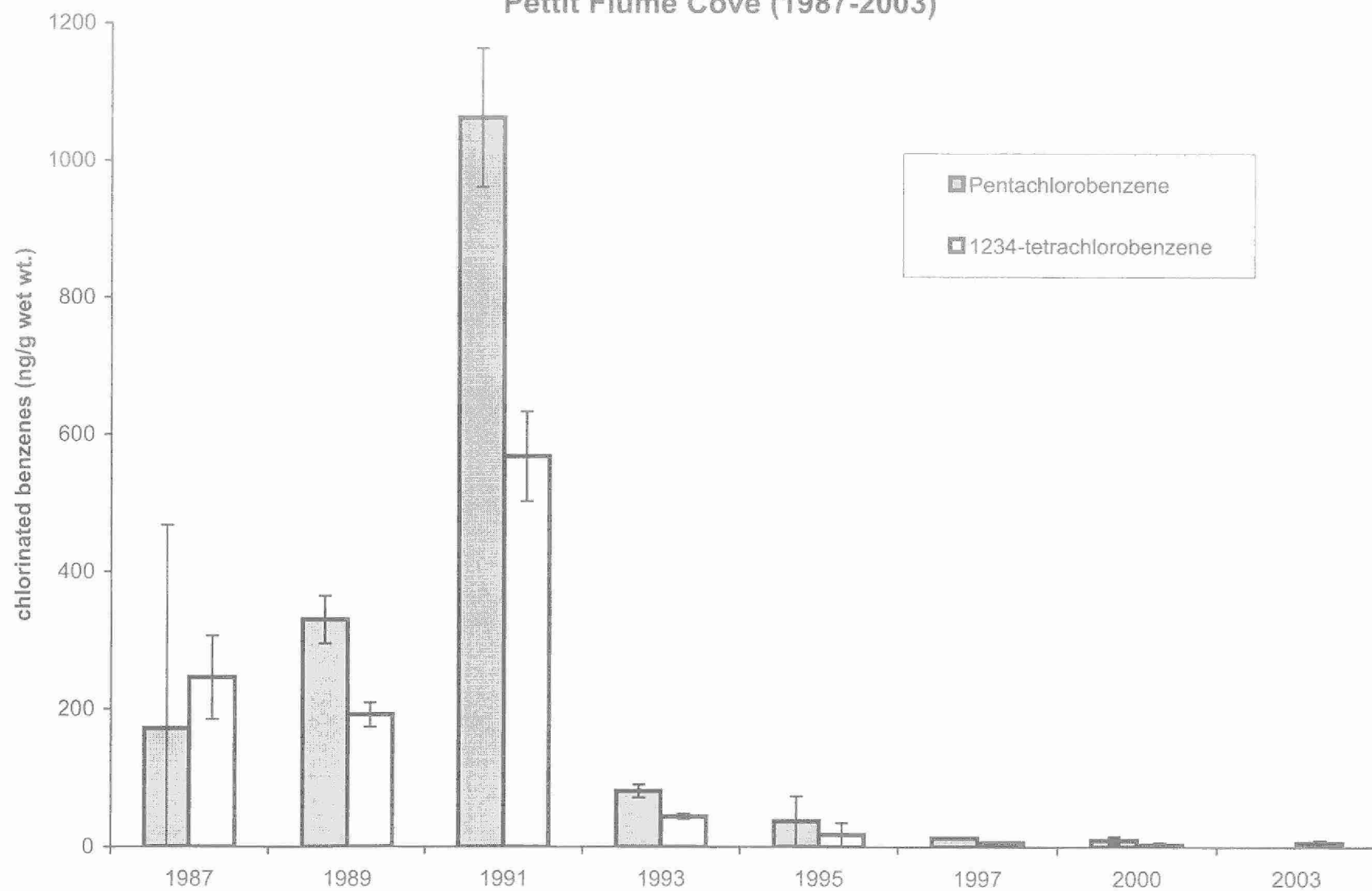
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Mean mussel tissue concentrations for chlorinated benzenes and 2,3,6- and 2,4,5-trichlorotoluene from the Occidental Sewer 003 site (Occidental's SPDES permitted outfall) have been variable during previous surveys. However, concentrations for both these groups of compounds have been relatively low in 1997, 2000 and 2003 compared with data collected between 1983 and 1995. 2,3,6- and 2,4,5-trichlorotoluene have been detected since 1983 in mussels deployed at the various outfalls associated with the Occidental Chemical Corporation property although not consistently at any one site with the exception of Sewer 003. The 2003 survey was the first time that it was not detected at this site since 1989. In contrast, HCBd has been consistently detected at Sewer 003 since 1993 and was also known to be present in Occidental's effluent (NRTC 1984).

The highest concentrations of HCBd were present in mussels deployed at the mouth of Gill Creek (mean 36 ng/g SD 1.4 ng/g). Hexachlorobutadiene has frequently been detected in caged mussels at this site in previous surveys, although at times the variability in tissue concentrations have been high. Concentrations in deployed mussels at Gill Creek have ranged from as low as 9 ng/g (SD 1 ng/g) in 1993 to 147 ng/g (SD 23.1 ng/g) in 1997. Hexachlorobutadiene was stored in waste sites which were known to leach contaminants into Gill Creek (NRTC 1984) which suggests that there could be a source here. Future mussel monitoring surveys will include additional sampling stations upstream of Gill Creek along the Niagara River shoreline to better define the area of contamination. 1,2,4,5-tetrachlorobenzene was also detected in all three mussels deployed at the mouth of Gill Creek.

Concentrations of chlorinated benzenes in mussels deployed at the Pettit Flume inlet cove have been low since 1995 relative to previous years of sampling before site remediation (Anderson *et al.* 1991; Richman 1992-2003). The Pettit Flume is a storm sewer that historically received waste water from the Occidental Chemical Corporation Durez Division and surrounding hazardous waste sites (Geologic Testing Consultants Ltd. 1984) (Appendix A4-Figure). Prior to the remediation of the cove and containment of contaminants at the waste site, the cove was filled with waste products which included chlorinated phenols, chlorotoluene, other organic and inorganic compounds and phenol tar containing chlorinated benzenes (Interagency Task Force on Hazardous Waste 1979; Raven 1991; US EPA and NYSDEC 2002). As well, high concentrations of dioxins and furans were routinely detected in sediment collected from the cove and in deployed mussels. Prior to 1995 there were high tissue concentrations of hexachlorobenzene, pentachlorobenzene and 1,2,3,4 tetrachlorobenzene. In 2003, only 1,2,3,4 tetrachlorobenzene, 1,2,3,5 tetrachlorobenzene and 2,3,6- and 2,4,5-trichlorotoluene were present at detectable concentrations in mussel tissue and concentrations were low relative to concentrations prior to remediation reinforcing the continued success of the remediation effort for chlorinated benzenes (Figure 6). The presence of these parameters was likely due to residual contamination in the flume. However, high concentrations of dioxins and furans were detected in deployed mussels and sediment collected from the cove in 1997, 2000 and again in 2003 suggesting that there is still an active source of dioxins and furans to the cove. This will be discussed in greater detail in the next section.

Figure 6: Chlorinated Benzenes (mean \pm SD) in Caged Mussels Deployed in the Pettit Flume Cove (1987-2003)



The 2004 data from Bloody Run Creek suggested that this area is a source of chlorinated benzenes to the Niagara River. One way analysis of variance and Tukey multiple comparison test showed that tissue concentrations of pentachlorobenzene were significantly higher in mussels deployed at the three sites along the Niagara River in the vicinity of Bloody Run Creek when compared with mussels deployed upstream and downstream of the site ($F=46.9$, $p<0.001$) (Appendix C). Since the data for hexachlorobenzene and hexachlorobutadiene were not normally distributed the Kruskal-Wallis one way analysis of variance on ranks was used and Tukeys multiple comparison test to assess differences in tissue concentrations between test sites. The results (Appendix C) showed significantly higher concentrations of hexachlorobenzene and hexachlorobutadiene at two stations (130 and 132) in the area of Bloody Run Creek when compared with the upstream site (station 18). Contaminants with the highest concentrations in mussels were pentachlorobenzene, hexachlorobenzene, 1,2,3,5-tetrachlorobenzene and 1,2,4-trichlorobenzene as well as hexachlorobutadiene (Table 4a; Figure 7).

Polycyclic Aromatic Hydrocarbons

The highest concentrations of PAHs in mussel tissue were present in mussels deployed at the mouths of storm sewers and urban creeks (Cayuga Creek, Two Mile Creek, Pettit Flume, mouth of the sewer discharging to the Niagara River downstream of Superior Lubricant). Concentrations of total PAHs ranged from 620 ng/g to 1,200 ng/g at these sites (Table 5). The likely sources of PAHs would be road and surface runoff to storm sewers that discharge to the creeks or through storm sewers directly as in the case of the Pettit Flume.

Concentrations ranging from 95 to 320 ng/g were present in mussels deployed in Lyons Creek, the Buffalo River, the Erie Canal, and Gill Creek. With the exception of one site, PAHs were not detected at any of the stations associated with the Occidental Chemical Company, or in mussels deployed at Gratwick Riverside Park, 102nd Street Landfill or the mouth of Gill Creek and NOTL. As well, PAHs were only detected sporadically at Fort Erie and in the Chippawa Channel and at the downstream site at Bloody Run Creek in 2004.

The highest concentrations and most frequently detected PAH compounds were benzo(b)fluoranthene, chrysene, flouranthene, and pyrene (Figure 8). However, chrysene was not detected in mussels deployed on the Canadian side of the river. The high molecular weight and low water solubility of compounds such as benzo(b)fluoranthene and chrysene suggest that these compounds may be more associated with suspended particles and taken up by the mussels through the digestive track rather than being absorbed through the gills. Flouranthene and pyrene are more soluble in water and may be available from the water column and suspended particulate matter (Piccardo *et al.* 2001).

Concentrations of PAHs in mussels in 2003 were similar to concentrations reported in 1997 (the last time PAHs were monitored), with the exception of the Pettit Flume, where concentrations of chrysene and flouranthene were higher in 1997. As well, Cayuga Creek

Figure 7: Chlorinated Compounds (mean \pm SD) in Caged Mussels Deployed Along the Shoreline of the Niagara River Near the Mouth of Bloody Run Creek, 2004

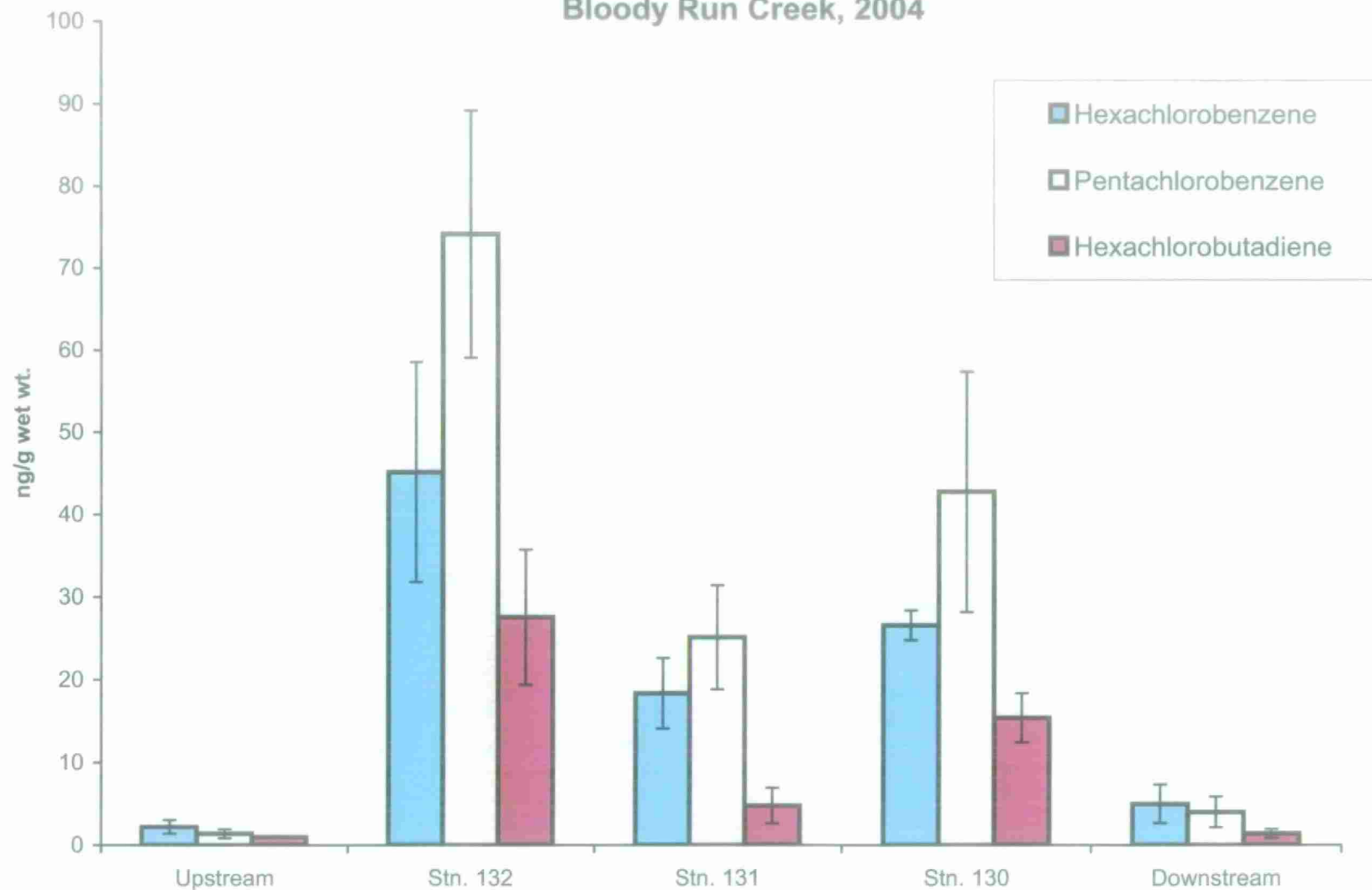


Table 5: Concentrations (ng/g wet wt.) of polycyclic aromatic hydrocarbons in caged mussels, Niagara River, 2003. An analyte <=W is designated as ".". Trace values "<T" are concentrations between "W" and 10 times "W"

Station Description	Station Number			Field Number	Acenaphthene 20<=W	Acenaphthylene 20<=W	Anthracene 20<=W	Benzo(a) anthracene 20<=W	Benzo(a) pyrene 40<=W	Benzo(b) fluoranthene 20<=W	Benzo(k) fluoranthene 20<=W	
Canadian Sites												
Fort Erie at Robertson St.	5	2	203	GL035723
	5	2	203	GL035724
	5	2	203	GL035725
Frenchmans Creek - Durez	5	15	19	GL035727	24	<T	.
	5	15	19	GL035728
	5	15	19	GL035729
Chippawa Channel	5	2	51	GL035744
	5	2	51	GL035745
	5	2	51	GL035746
Lyons Creek	5	15	20	GL035731	.	.	.	27	<T	48	<T	.
	5	15	20	GL035732	27	<T	.
	5	15	20	GL035733	.	.	.	26	<T	54	<T	.
Niagara-on-the-Lake	11	2	9	GL035751
	11	2	9	GL035752
	11	2	9	GL035753
American Sites												
Buffalo River	5	2	220	GL035719	28	<T	.
	5	2	220	GL035720
	5	2	220	GL035721	34	<T	.
Tonawanda Channel - upstream of Two Mile Creek	5	2	92	GL035715
	5	2	92	GL035716
	5	2	92	GL035717
Two Mile Creek	5	2	197	GL035705	140	.	40 <T
	5	2	197	GL035706	80	<T	.
	5	2	197	GL035707	.	.	.	40	<T	220	.	60 <T
Holiday Park - upstream Exolon	5	15	33	GL035697
	5	15	33	GL035698	60	<T	.
	5	15	33	GL035699	80	<T	.
Holiday Park - downstream Exolon	5	15	34	GL035701	40	<T	.
	5	15	34	GL035702
	5	15	34	GL035703	60	<T	.
Pettit Flume - upstream	5	2	185	GL035681
	5	2	185	GL035682
	5	2	185	GL035683
Pettit Flume - Site B	5	2	186	GL035690	.	.	.	40	<T	180	.	40 <T
	5	2	186	GL035691	160	.	.
	5	2	186	GL035692	.	.	.	40	<T	140	.	40 <T
Pettit Flume - downstream	5	2	187	GL035693
	5	2	187	GL035694
	5	2	187	GL035695
Mouth of Sewer - downstream Superior Lubricant	5	2	4	GL035622	.	.	.	40	<T	200	.	60 <T
	5	2	4	GL035623	100	.	40 <T
	5	2	4	GL035624	.	.	.	40	<T	180	.	60 <T

Table 5: Concentrations (ng/g wet wt.) of polycyclic aromatic hydrocarbons in caged mussels, Niagara River, 2003. An analyte $\leq W$ is designated as ".". Trace values "<T" are concentrations between "W" and 10 times "W"

Station Description	Station Number			Field Number	Acenaphthene 20<=W	Acenaphthylene 20<=W	Anthracene 20<=W	Benzo(a) anthracene 20<=W	Benzo(a) pyrene 40<=W	Benzo(b) fluoranthene 20<=W	Benzo(k) fluoranthene 20<=W
Gratwick/Riverside Park - upstream	5	2	31	GL035626
Gratwick/Riverside Park	5	2	31	GL035627
	5	2	199	GL035628
	5	2	199	GL035629
	5	2	199	GL035630
Cayuga Creek	5	15	31	GL035618	.	.	.	40	<T	160	40
	5	15	31	GL035619	.	.	.	40	<T	200	60
102nd Street - upstream	5	2	93	GL035634
	5	2	93	GL035635
	5	2	93	GL035636
102nd Street - outfall	5	5	23	GL035637
	5	5	23	GL035638
	5	5	23	GL035639
Occidental - upstream of storm sewer A	5	2	47	GL035678
	5	2	47	GL035679
	5	2	47	GL035680
Occidental - storm sewer A	5	2	46	GL035675
	5	2	46	GL035676
	5	2	46	GL035677
Occidental - storm sewer B	5	2	94	GL035672
	5	2	94	GL035673
	5	2	94	GL035674
Occidental - between storm sewer B & C	5	2	45	GL035669
	5	2	45	GL035670
	5	2	45	GL035671
Occidental - storm sewer C	5	2	44	GL035666
	5	2	44	GL035667
	5	2	44	GL035668
Occidental - downstream of storm sewer C	5	2	43	GL035663
	5	2	43	GL035664
	5	2	43	GL035665
Occidental Sewer 003	5	2	42	GL035649
	5	2	42	GL035650
	5	2	42	GL035651
Occidental - storm sewer S&N area	5	2	40	GL035646
	5	2	40	GL035647
	5	2	40	GL035648
Gill Creek - upstream of outfall	5	2	37	GL035612
	5	2	37	GL035613
Gill Creek - downstream of outfall	5	2	37	GL035614
	5	2	37	GL035615
	5	2	37	GL035616
Gill Creek - upstream within the creek	5	15	22	GL035603	60	<T
	5	15	22	GL035605
Bloody Run Creek - upstream	11	2	18	GL035643
	11	2	18	GL035644
	11	2	18	GL035645
Bloody Run Creek - downstream	11	2	25	GL035640
	11	2	25	GL035641
	11	2	25	GL035642
Balsam Lake - control	18	1	1	GL035760
	18	1	1	GL035761
	18	1	1	GL035762

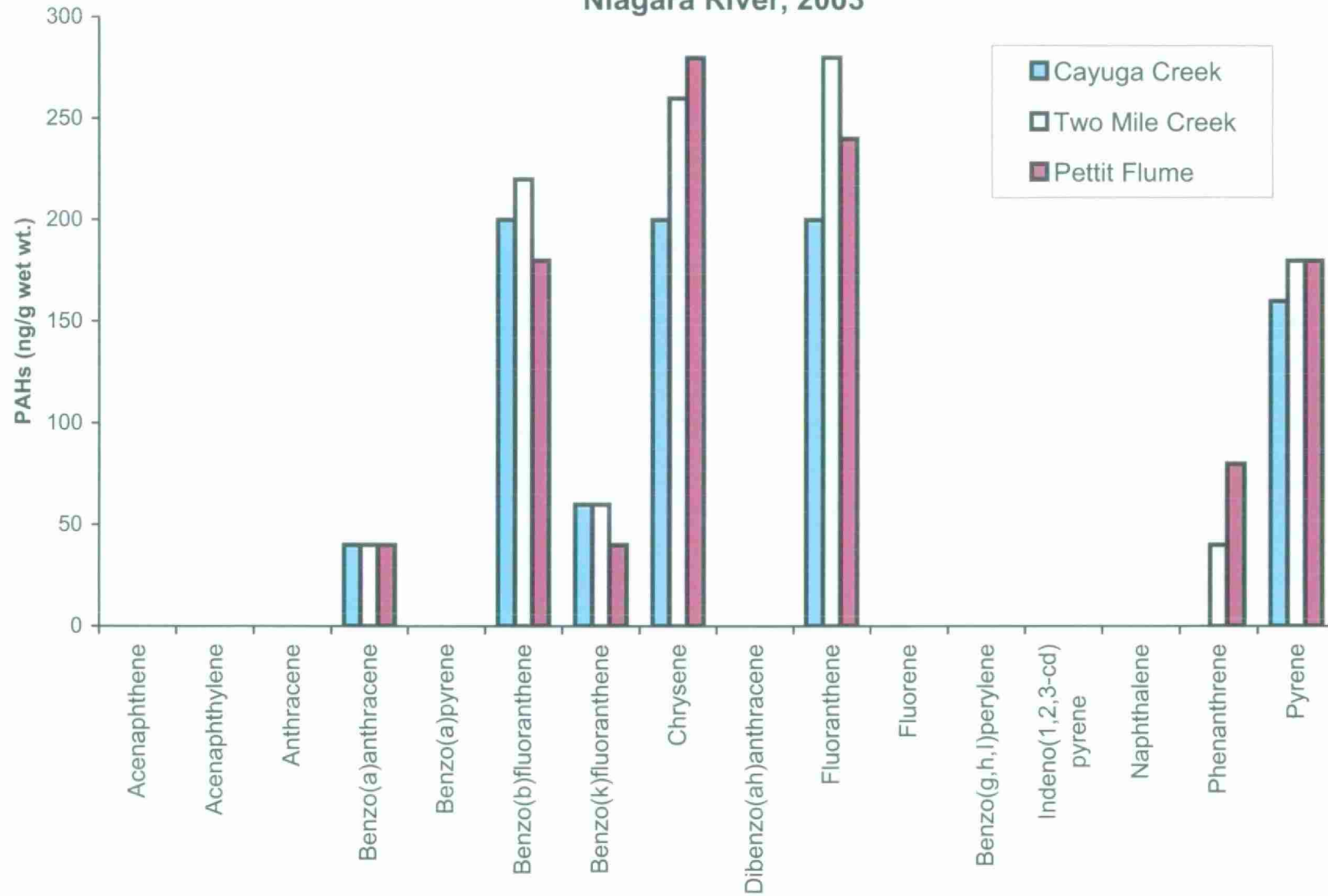
Table 5: Concentrations (ng/g wet wt.) of polycyclic aromatic hydrocarbons in caged mussels, Niagara River, 2003. An analyte <=W is designated as ".". Trace values "<T" are concentrations between "W" and 10 times "W"

Station Description	Station Number			Chrysene 20<=W	Dibenzo(ah) anthracene 40<=W	Fluoranthene 20<=W	Fluorene 20<=W	Benzo(g,h,i) perylene 40<=W	Indeno(1,2,3-cd) pyrene 40<=W	Naphthalene 20<=W	Phenanthrene 20<=W	Pyrene 20<=W	Total PAH
Canadian Sites													
Fort Erie at Robertson St.	5	2	203
	5	2	203
	5	2	203	.	.	37	<T	.	.	.	25	<T	114
Frenchmans Creek - Durez	5	15	19
	5	15	19
	5	15	19	.	.	25	<T	25	50
Chippawa Channel	5	2	51
	5	2	51
	5	2	51	.	.	38	<T	31	69
Lyons Creek	5	15	20	.	.	68	<T	120	263
	5	15	20	.	.	25	<T	43	95
	5	15	20	.	.	58	<T	100	238
Niagara-on-the-Lake	11	2	9
	11	2	9
	11	2	9
American Sites													
Buffalo River	5	2	220	57	<T	.	22	<T	.	.	.	80	187
	5	2	220	29	<T	40	69
	5	2	220	56	<T	.	21	70	181
Tonawanda Channel - upstream of Two Mile Creek	5	2	92
	5	2	92	.	.	23	<T	22	45
	5	2	92
Two Mile Creek	5	2	197	180	.	180	40	<T	700
	5	2	197	160	.	220	160	620
	5	2	197	260	.	280	40	<T	1080
Holiday Park - upstream Exolon	5	15	33	40	<T	.	80	<T	.	.	.	60	180
	5	15	33	60	<T	.	60	<T	.	.	.	40	220
	5	15	33	80	<T	.	100	60	320
Holiday Park - downstream Exolon	5	15	34	60	<T	.	60	<T	.	.	.	40	200
	5	15	34	40	<T	.	40	<T	.	.	.	40	120
	5	15	34	80	<T	.	80	<T	.	.	.	60	280
Pettit Flume - upstream	5	2	185
	5	2	185
	5	2	185
Pettit Flume - Site B	5	2	186	280	.	240	80	<T	1040
	5	2	186	280	.	280	120	220	1060
	5	2	186	220	.	180	60	<T	820
Pettit Flume - downstream	5	2	187
	5	2	187
	5	2	187
Mouth of Sewer - downstream Superior Lubricant	5	2	4	220	.	320	.	.	80	<T	.	80	1200
	5	2	4	160	.	200	40	<T	660
	5	2	4	200	.	280	.	.	80	<T	.	60	1060

Table 5: Concentrations (ng/g wet wt.) of polycyclic aromatic hydrocarbons in caged mussels, Niagara River, 2003. An analyte $\leq W$ is designated as ".". Trace values " $<T$ " are concentrations between " W " and 10 times " W ".

[illegible]

Figure 8: PAHs (n=1) in Caged Mussels Deployed at Sites in the
Niagara River, 2003



(last monitored for PAHs in 1995) had higher concentrations of chrysene, flouranthene, and pyrene in 2003. Some variability in tissue concentrations would be expected between survey years given the sporadic nature of the non-point source inputs (road and surface runoff, storm sewers, etc.).

Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans

In 2003, dioxins and furans were analysed in sediment collected from eleven stations, and in one composite mussel sample (four mussels per site), from each of six stations. Data presented for mussels deployed at Bloody Run Creek and for the Balsam Lake control mussels are from the 2004 survey (Table 6, 6a & 7).

Toxicity Equivalency Factors (TEFs) have been used as a measure to express the toxicity of different dioxins and furans and dioxin-like PCBs on a common basis. TEFs were assigned to individual dioxins, furans and dioxin-like PCBs on the basis of how toxic they were in comparison with the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (T4CDD), which was assigned the value of 1.0. When concentrations of individual isomers are converted to toxicity equivalents of 2,3,7,8-T4CDD they are then summed to yield a total toxic equivalent (TEQ). The World Health Organization TEFs for the protection of humans and mammals from August 1997 were used for the calculations for both sediment and mussels (van den Berg *et al.* 1998) to be consistent with earlier reports. However, TEQs calculated using TEFs for the protection of fish and birds were also provided in the data tables. Where appropriate, the calculated TEQs can be compared with sediment quality guidelines and tissue residue guidelines, to help put the values in perspective. Ontario does not have a Sediment Quality Guideline (SQG) for dioxins and furans at present; however, the Canadian Environmental Quality Guideline "probable effect level" has been set at 21.5 pg/g TEQ (CCME, 2001). This value was calculated using TEF for the protection of fish. The New York State tissue guideline for the protection of piscivorous wildlife is 3 pg/g (Newell *et al.* 1987).

Dioxins and furans were not detected in the Balsam Lake control mussels (Table 6a). The total TEQ for Balsam Lake mussels was 0.1 pg/g (using the mammalian TEF) which was due entirely to the presence of dioxin-like PCBs.

Dioxins and furan concentrations in sediment collected from Canadian sites were low. The total TEQ for sediment collected from NOTL was 9 pg/g which was similar to concentrations measured in 1993 and 1995 (TEQ:14.8 and 14.2 pg/g respectively) (Table 7; Figure 9). Dioxin-like PCBs were low and contributed only 9% to the total TEQ. Sediment from Lyons Creek, had a total TEQ of 17 pg/g with 25% of the total (4 pg/g) due to dioxin-like PCBs. Mussel data from these sites were unavailable due to a laboratory error in sample processing.

The TEQs for the sediment samples from Cayuga Creek and Two Mile Creek were 70 and 81 pg/g respectively in 2003. In 1995 (the last time sediment was collected from this site), the TEQ concentration in Cayuga Creek was lower at 18 pg/g. Although the sediment TEQ

Table 6: Concentrations of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like PCBs in mussels deployed in the Niagara River, 2003. n=1 (composite of four mussels).

Station Description Station Number Field Number Retrieval Date	Gill Creek (upstream) 5-15-22 GL045407 12-Aug-03 pg/g wet wt.		Cayuga Creek 5-15-31 GL045408 12-Aug-03 pg/g wet wt.		Exalon (upstream) 5-15-33 GL045410 14-Aug-03 pg/g wet wt.	
2378-tetrachlorofuran	4.3		2.2		0.88	<
12378-pentachlorofuran	0.64	<	0.41	<	0.4	<
23478-pentachlorofuran	1	<	0.51	<	0.49	<
123478-hexachlorofuran	1.5		0.3	<	0.3	<
123678-hexachlorofuran	0.55	<	0.3	<	0.3	<
123789-hexachlorofuran	0.5	<	0.4	<	0.5	<
234678-hexachlorofuran	0.4	<	0.3	<	0.3	<
1234678-heptachlorofuran	2.9	<	2.3	<	1.5	<
1234789-heptachlorofuran	0.47	<	0.3	<	0.5	<
Octachlorofuran	1.9	<	2	<	2	<
2378-tetrachlorodioxin	1	<	3.5	<	2.2	<
12378-pentachlorodioxin	0.62	<	0.5	<	0.6	<
123478-hexachlorodioxin	0.5	<	0.7	<	0.6	<
123678-hexachlorodioxin	0.81	<	0.6	<	0.6	<
123789-hexachlorodioxin	0.5	<	0.7	<	0.6	<
1234678-heptachlorodioxin	2.6	<	2.5	<	1.2	<
Octachlorodioxin	15		13		6.9	<
Dioxin/furan TEQ (mammals)	0.6		0.2		0	
PCB081	6	<	2.6	<	2.7	
PCB077	130		51		79	
PCB123	110		97		63	
PCB118	1900		1900		1300	
PCB114	69		39		27	
PCB105	670		680		410	
PCB126	9.8		5		3.7	
PCB167	74		62		37	
PCB156	190		170		82	
PCB157	43		40		19	
PCB169	0.1	<	0.46	<	0.2	<
PCB189	24		9.6		7.2	
DLPCB TEQ (mammals)	1.4		0.9		0.6	
Total TEQ (pg/g dry wt.) - mammals	2.0		1.1		0.6	
% DLPCB of total TEQ	71%		80%		100%	
Total TEQ (pg/g dry wt.) - fish	0.44		0.16		0.04	
Total TEQ (pg/g dry wt.) - birds	12.05		5.36		4.66	
Percent Lipid	0.35		0.63		0.47	
Tetrachlorofuran; total						
Pentachlorofuran; total						
Hexachlorofuran; total						
Heptachlorofuran; total						
Tetrachlorodioxin; total						
Pentachlorodioxin; total						
Hexachlorodioxin; total						
Heptachlorodioxin; total						

* Number of isomers detected in the congener group
"<" Compound was below the detection limit
Congener groups were only available for the Pettit Flume

Table 6: Concentrations of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like PCBs in mussels deployed in the Niagara River, 2003. n=1 (composite of four mussels).

Station Description Station Number Field Number Retrieval Date	Pettit Flume (upstream) 5-02-185 GL045415 14-Aug-03 pg/g wet wt.		Pettit Flume (downstream) 5-02-187 GL045416 14-Aug-03 pg/g wet wt.		Pettit Flume 5-02-186 GL045417 14-Aug-03 pg/g wet wt.	
2378-tetrachlorofuran	0.42	<	1.6	<	91	
12378-pentachlorofuran	0.2	<	0.44	<	17	
23478-pentachlorofuran	0.21	<	1.1	<	43	
123478-hexachlorofuran	0.3	<	3.1	<	140	
123678-hexachlorofuran	0.3	<	0.83	<	35	
123789-hexachlorofuran	0.4	<	0.4	<	4	<
234678-hexachlorofuran	0.3	<	0.3	<	9.7	
1234678-heptachlorofuran	0.33	<	3.9		120	
1234789-heptachlorofuran	0.3	<	0.3	<	4.7	
Octachlorofuran	1.1	<	3.7	<	69	
2378-tetrachlorodioxin	1.1	<	1.1	<	7.7	
12378-pentachlorodioxin	0.3	<	0.5	<	5.9	
123478-hexachlorodioxin	0.4	<	0.4	<	2	<
123678-hexachlorodioxin	0.4	<	0.4	<	4.3	
123789-hexachlorodioxin	0.4	<	0.4	<	2.3	
1234678-heptachlorodioxin	0.41	<	0.7	<	4.7	
Octachlorodioxin	1.6	<	2.6	<	6.9	<
Dioxin/furan TEQ (mammals)	0		0.4		65.5	
PCB081	0.99	<	2	<	3.9	
PCB077	23		46		19	
PCB123	9.4		29		57	
PCB118	180		540		490	
PCB114	5.7		18		43	
PCB105	72		200		160	
PCB126	0.84	<	2.1	<	7.4	
PCB167	5.1		16		44	
PCB156	11		44		120	
PCB157	2.5		10		18	
PCB169	0.15	<	0.1	<	1.1	<
PCB189	1.5		3.9		21	
DLPCB TEQ (mammals)	0.04		0.1		0.9	
Total TEQ (pg/g dry wt.) - mammals	0.04		0.5		66.4	
% DLPCB of total TEQ	100%		25%		1%	
Total TEQ (pg/g dry wt.) - fish	0.004		0.36		60.34	
Total TEQ (pg/g dry wt.) - birds	1.16		2.68		171.42	
Percent Lipid	0.47		0.7		0.44	
Tetrachlorofuran; total	1.5	14*	14	116	670	118
Pentachlorofuran; total	0.49	11	7.5	18	510	110
Hexachlorofuran; total	0.2	<	6.8	15	370	18
Heptachlorofuran; total	0.4	<	3.9	11	160	13
Tetrachlorodioxin; total	20	15	19	15	580	111
Pentachlorodioxin; total	0.71	11	1.8	12	140	18
Hexachlorodioxin; total	0.2	<	0.3	<	43	17
Heptachlorodioxin; total	0.4	<	0.7	<	8	12

Table 6a: Concentrations of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzo furans and dioxin-like PCBs in mussels deployed in the Niagara River near Bloody Run Creek, 2004. n=1 (composite of four mussels).

Station Description Station Number Field Number Retrieval Date	Balsam Lake Control 18-01-01 GL043007 12-Jul-04 pg/g wet wt.	BRC - Downstream 11-02-25 GL043014 04-Aug-04 pg/g wet wt.	BRC 11-02-130 GL043021 04-Aug-04 pg/g wet wt.	BRC 11-02-131 GL043028 04-Aug-04 pg/g wet wt.	BRC 11-02-132 GL043035 04-Aug-04 pg/g wet wt.	BRC - Upstream 11-02-18 GL043049 04-Aug-04 pg/g wet wt.
2378-tetrachlorofuran	0.9	< 1	< 1.4	1.1	2	1
12378-pentachlorofuran	0.5	< 0.7	< 1	< 0.6	< 0.9	< 0.8
23478-pentachlorofuran	1	< 0.9	< 1	< 0.9	< 1	< 0.8
123478-hexachlorofuran	0.2	< 0.3	< 1	< 1	< 0.7	< 0.5
123678-hexachlorofuran	0.2	< 0.2	< 0.5	< 0.5	< 0.3	< 0.3
123789-hexachlorofuran	0.3	< 0.3	< 0.5	< 0.3	< 0.6	< 0.8
234678-hexachlorofuran	0.5	< 0.2	< 0.6	< 0.4	< 0.3	< 0.5
1234678-heptachlorofuran	0.4	< 1	< 0.7	< 2.1	< 0.9	< 1
1234789-heptachlorofuran	0.3	< 0.5	< 0.2	< 0.4	< 0.6	< 0.3
Octachlorofuran	0.8	< 1.3	0.8	< 2.6	0.5	< 2
2378-tetrachlorodioxin	3	< 8.9	40	< 41	37	3
12378-pentachlorodioxin	1	< 1	< 4	< 0.6	< 9.4	1
123478-hexachlorodioxin	0.9	< 0.7	< 1	< 0.5	< 1	< 0.5
123678-hexachlorodioxin	0.9	< 0.9	< 2	< 3.5	2.8	2
123789-hexachlorodioxin	0.8	< 0.8	< 2	< 0.6	< 1	< 1
1234678-heptachlorodioxin	0.5	< 0.9	< 2	< 5.3	3.2	1
Octachlorodioxin	1	< 2	< 3	< 5.5	3.9	2
Dioxin/furan TEQ (mammals)	0	9	0.1	42	47	0
PCB081	0.2	< 3.3	6.7	10	12	1
PCB077	2	< 21	37	76	85	12
PCB123	2.6	15	24	32	28	9.8
PCB118	49	270	340	550	520	160
PCB114	1	< 14	26	47	43	6.8
PCB105	17	130	160	290	270	75
PCB126	0.95	2.4	4.5	6.8	7.6	2.1
PCB167	4.8	13	11	19	17	7.8
PCB156	8.2	19	19	29	27	16
PCB157	1	< 6.9	9.6	14	12	3.4
PCB169	0.5	< 0.4	< 0.5	< 0.68	1.1	0.3
PCB189	1.5	3.2	2.9	4	3.3	3.2
DLPCB TEQ (mammals)	0.1	0.3	0.5	0.8	0.1	0.3
Total TEQ (pg/g) - mammals	0.1	9.2	0.7	42.4	47.6	0.3
% DLPCB of total TEQ	100%	3.3%	79%	1.9%	1.9%	100%
Total TEQ (pg/g) - fish	0.01	8.9	0.1	41.2	46.5	0.01
Total TEQ (pg/g) - birds	0.1	10.5	4.4	47.7	52.7	0.8
percent lipid	0.33	0.28	0.46	0.53	0.31	1.1
Tetrachlorofuran; total	0.9	< 3.6	12* 6.3	12 20	19 2.9	11 1
Pentachlorofuran; total	1	< 1.5	11 1	< 8.6	14 5	12 0.8
Hexachlorofuran; total	0.5	< 0.59	11 1	< 1	< 1	< 0.8
Heptachlorofuran; total	0.4	< 1	< 0.7	< 2.1	11 0.9	< 1
Tetrachlorodioxin; total	3	< 8.9	11 40	< 41	11 37	11 3
Pentachlorodioxin; total	1	< 1	< 1	< 5.8	12 9.4	11 1
Hexachlorodioxin; total	0.9	< 0.9	< 2.2	12 9.2	13 5.6	12 2
Heptachlorodioxin; total	0.5	< 0.9	< 2	< 8.4	12 4.6	12 1

* Number of isomers detected in the congener group

"<" Compound was below the detection limit

Table 7: Concentrations of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like PCBs in sediment collected from the Niagara River, 2003

Station Description	Pettit Flume (upstream)		Pettit Flume Site B		Pettit Flume (downstream)		Two Mile Creek	
Station Number	5-2-185		5-2-186		5-2-187		5-2-197	
Field Number	GL035806		GL035807		GL035808		GL035810	
Retrieval Date	14-Aug-03		14-Aug-03		14-Aug-03		14-Aug-03	
	pg/g dry wt.		pg/g dry wt.		pg/g dry wt.		pg/g dry wt.	
2378-tetrachlorofuran	9.4		3800		690		30	
12378-pentachlorofuran	2.6		1800		190		7	
23478-pentachlorofuran	5		3900		840		13	
123478-hexachlorofuran	21		49000		10000		42	
123678-hexachlorofuran	5.8		8600		1300		14	
123789-hexachlorofuran	1	<	89		14		1	<
234678-hexachlorofuran	2.6		2200		350		10	
1234678-heptachlorofuran	70		130000		27000		170	
1234789-heptachlorofuran	4		5600		1200		13	
Octachlorofuran	140		340000		78000		390	
2378-tetrachlorodioxin	24		370		30		22	
12378-pentachlorodioxin	3.7		800		53		6	
123478-hexachlorodioxin	4		650		64		8.7	
123678-hexachlorodioxin	15		1400		130		39	
123789-hexachlorodioxin	11		1200		85		31	
1234678-heptachlorodioxin	140		6000		740		420	
Octachlorodioxin	1400		13000		3100		2900	
Dioxin/furan TEQ (mammals)	40		11,355		2,073		59	
PCB081	28		100		28		110	
PCB077	860		640		630		3200	
PCB123	250		1200		200		1700	
PCB118	4900		9700		4200		28000	
PCB114	160		1200		250		780	
PCB105	2500		3600		1800		15000	
PCB126	32		230		33		150	
PCB167	220		1500		230		1800	
PCB156	520		4000		670		3600	
PCB157	130		550		130		1100	
PCB169	2.5		44		5.3		9.9	
PCB189	77		1000		160		390	
DLPCB TEQ (mammals)	4.5		28.0		4.6		22.7	
Total TEQ (pg/g dry wt.) - mammals	44		11,383		2,078		81	
% DLPCB of total TEQ	10%		0.3%		0.2%		28%	
Total TEQ (pg/g dry wt.) - fish	37		11,137		2,038		52	
TOC - mg/g	34		120		20		65	
Tetrachlorofuran; total	78	I21*	25000	I22	4700	I19	200	I20
Pentachlorofuran; total	82	I12	40000	I13	7700	I16	230	I14
Hexachlorofuran; total	99	I12	110000	I15	19000	I15	320	I11
Heptachlorofuran; total	110	I4	140000	I4	31000	I4	350	I4
Tetrachlorodioxin; total	54	I7	22000	I14	960	I15	120	I11
Pentachlorodioxin; total	37	I8	17000	I12	980	I12	68	I12
Hexachlorodioxin; total	110	I7	25000	I8	1700	I8	260	I8
Heptachlorodioxin; total	270	I2	10000	I2	1300	I2	720	I2

* Number of isomers detected in the congener group

"<" Compound was below the detection limit

NDLA - sample spoiled in laboratory accident

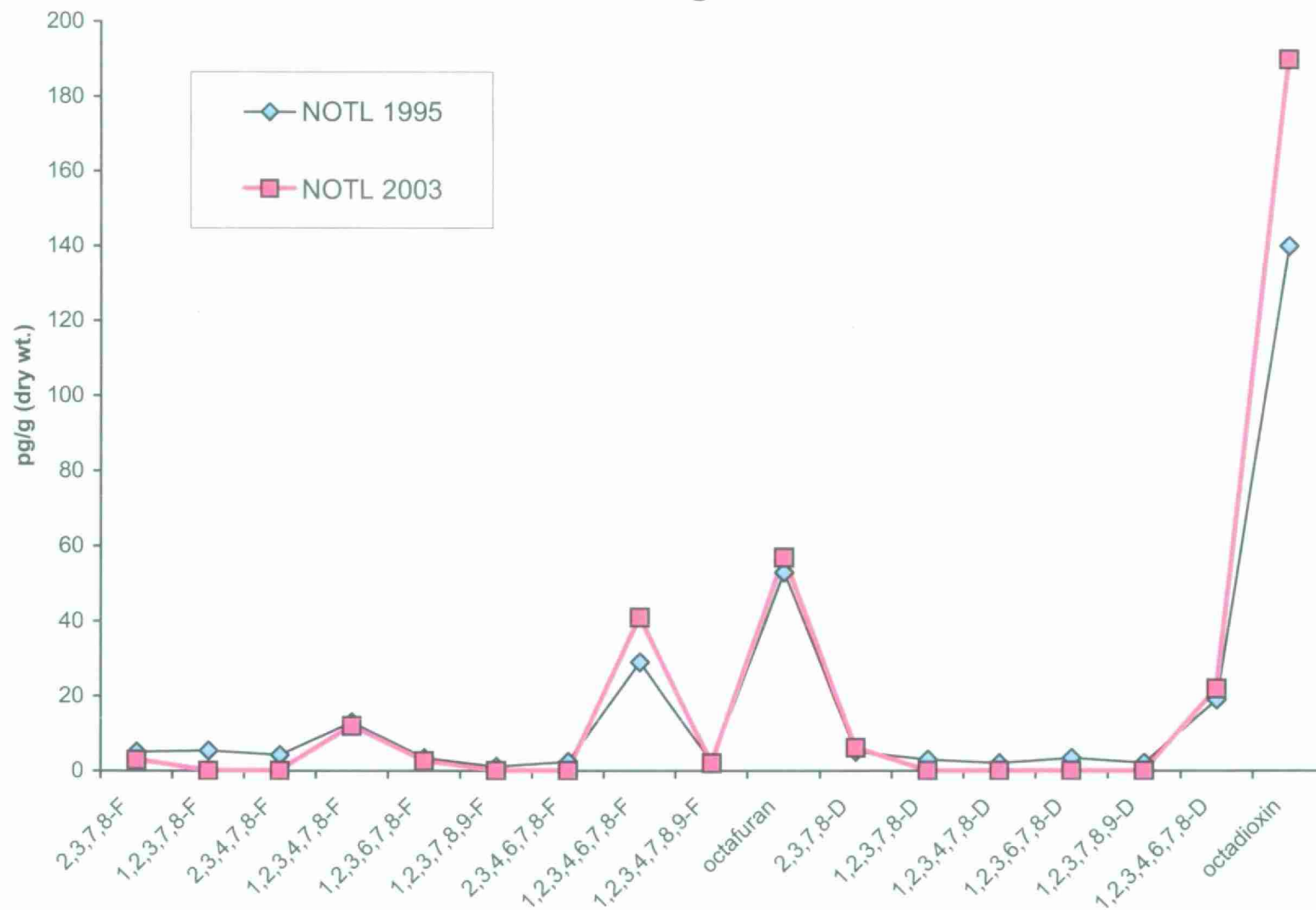
Table 7: Concentrations of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like PCBs in sediment collected from the Niagara River, 2003

Station Description	Lyons Creek		Gill Creek (upstream within creek)		Cayuga Creek		Holiday Park (upstream of Exolon)	
Station Number	5-15-20		5-15-22		5-15-31		5-15-33	
Field Number	GL035811		GL035800		GL035802		GL035809	
Retrieval Date	15-Aug-03		12-Aug-03		12-Aug-03		14-Aug-03	
	pg/g dry wt.		pg/g dry wt.		pg/g dry wt.		pg/g dry wt.	
2378-tetrachlorofuran	2.9		69		20		10	
12378-pentachlorofuran	0.6		23		7.8		2.7	
23478-pentachlorofuran	1.4		24		8.8		6.7	
123478-hexachlorofuran	7.3		370		45		42	
123678-hexachlorofuran	1.8		50		10		7.8	
123789-hexachlorofuran	0.6	<	2.8		3	<	1	<
234678-hexachlorofuran	0.85		7.5		9.8		2.5	
1234678-heptachlorofuran	24		380		150		58	
1234789-heptachlorofuran	1.5		170		15		8.5	
Octachlorofuran	43		1200		280		160	
2378-tetrachlorodioxin	2.9		4.4		34		61	
12378-pentachlorodioxin	1.6		6.6		5.9		3.1	
123478-hexachlorodioxin	3.3		18		8.3		4.6	
123678-hexachlorodioxin	7.9		70		22		43	
123789-hexachlorodioxin	7.5		45		34		27	
1234678-heptachlorodioxin	220		990		250		240	
Octachlorodioxin	18000		8400		1800		800	
Dioxin/furan TEQ (mammals)	13		104		64		84	
PCB081	41		100		18		40	
PCB077	1300		2700		400		420	
PCB123	330		510		400		130	
PCB118	5600		13000		9100		2500	
PCB114	210		530		230		130	
PCB105	3400		6800		4100		1300	
PCB126	29		120		41		24	
PCB167	140		470		470		110	
PCB156	330		1300		1200		250	
PCB157	95		280		300		76	
PCB169	0.74		7		6	<	3	
PCB189	34		190		86		29	
DLPCB TEQ (mammals)	4.3		15.5		6.4		3.1	
Total TEQ (pg/g dry wt.) - mammals	17		119		70		88	
% DLPCB of total TEQ	25%		13%		9%		4%	
Total TEQ (pg/g dry wt.) - fish	9		88		59		77	
TOC - mg/g	28		17		82		33	
Tetrachlorofuran; total	19	I15	340	I18	130	I16	68	I17
Pentachlorofuran; total	23	I10	310	I15	210	I10	94	I12
Hexachlorofuran; total	34	I8	730	I13	230	I7	130	I11
Heptachlorofuran; total	53	I4	750	I4	300	I4	99	I4
Tetrachlorodioxin; total	6.7	I4	42	I8	85	I6	78	I5
Pentachlorodioxin; total	15	I9	110	I9	54	I5	45	I5
Hexachlorodioxin; total	82	I8	410	I8	210	I8	230	I8
Heptachlorodioxin; total	500	I2	1400	I2	440	I2	380	I2

Table 7: Concentrations of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like PCBs in sediment collected from the Niagara River, 2003

Station Description	Niagara-on-the-Lake		Bloody Run Creek		Bloody Run Creek (upstream)	
Station Number	11-2-9		11-2-17		11-2-18	
Field Number	GL035813		GL035803		GL035804	
Retrieval Date	15-Aug-03		13-Aug-03		13-Aug-03	
	pg/g dry wt.		pg/g dry wt.		pg/g dry wt.	
2378-tetrachlorofuran	2.9		2000		17	
12378-pentachlorofuran	2	<	780		3.3	
23478-pentachlorofuran	2	<	4500		9.2	
123478-hexachlorofuran	12		38000		59	
123678-hexachlorofuran	2.6		6300		13	
123789-hexachlorofuran	1	<	140		4	<
234678-hexachlorofuran	0.9	<	870		2.6	
1234678-heptachlorofuran	41		26000		82	
1234789-heptachlorofuran	2		5100		13	
Octachlorofuran	57		110000		200	
2378-tetrachlorodioxin	6.2		95000		160	
12378-pentachlorodioxin	1	<	1300		3.9	
123478-hexachlorodioxin	1	<	4600		4	<
123678-hexachlorodioxin	2	<	73000		78	
123789-hexachlorodioxin	2	<	71000		41	
1234678-heptachlorodioxin	22		320000		360	
Octachlorodioxin	190		230000		240	
Dioxin/furan TEQ (mammals)	9		121,725		194	
PCB081	4.8		NDLA		68	
PCB077	200		NDLA		910	
PCB123	43		35000		200	
PCB118	1200		580000		4100	
PCB114	27		90000		220	
PCB105	360		380000		2500	
PCB126	4.3		NDLA		37	
PCB167	29		37000		94	
PCB156	65		71000		180	
PCB157	19		32000		59	
PCB169	0.3	<	NDLA		3.7	
PCB189	8.2		10000		20	
DLPCB TEQ (mammals)	0.7		197.4		4.8	
Total TEQ (pg/g dry wt.) - mammals	9		121,922		199	
% DLPCB of total TEQ	7%		0.2%		2%	
Total TEQ (pg/g dry wt.) - fish	8		107,608		180	
TOC - mg/g	7		22		5	
Tetrachlorofuran; total	23	115	11000	119	110	116
Pentachlorofuran; total	20	19	43000	116	130	110
Hexachlorofuran; total	30	16	76000	114	150	119
Heptachlorofuran; total	52	14	47000	14	130	14
Tetrachlorodioxin; total	13	14	97000	19	170	13
Pentachlorodioxin; total	6.7	13	25000	112	48	14
Hexachlorodioxin; total	22	13	350000	18	290	15
Heptachlorodioxin; total	51	12	440000	12	510	12

Figure 9: Dioxin and Furan Isomer Patterns in Sediment Collected From Niagara-on-the-Lake



concentration suggested some dioxin/furan contamination, the TEQ concentration in caged mussels was low for Cayuga Creek (1.12 pg/g), and up to 80% of the TEQ was due to dioxin-like PCBs. However, dioxin-like PCBs in sediment only accounted for 9% of the total TEQ. Mussel data for Two Mile Creek were unavailable. Concentrations in the sediment were similar to concentrations measured in 2000 (81 pg/g). Twenty-eight percent of the total TEQ was due to dioxin-like PCB contamination.

The sediment collected from Gill Creek is of particular interest; in 2000 the TEQ was 103 pg/g similar to concentrations measured in 2003 (119 pg/g). This data suggests the possibility of a recent source of dioxins and furans since dredging of the area in 1998 would have presumably removed any contaminated sediment. However, we do not have data prior to 2000 to confirm this hypothesis. The bioavailability of dioxins and furans was low (2 pg/g TEQ) with 71% of the total TEQ in mussels due to dioxin-like PCBs. In contrast, only 13% of the total TEQ for sediment was due to dioxin-like PCB contamination.

Sediment collected from the Erie Canal also indicated dioxin and furan contamination with a total TEQ of 88 pg/g (dioxin-like PCBs - 4 pg/g TEQ). This was the first year that sediment was collected from this site. The total TEQ for mussels was low (0.62 pg/g) and entirely due to the bioaccumulation of dioxin-like PCBs.

Although the sediment concentrations for dioxins and furans vary between the stations, the isomer patterns were similar for all stations in the survey with the exception of Bloody Run Creek and the Pettit Flume (described below). These sites have unique patterns related to their sources (Figures 9 to 11 and 13).

Bloody Run Creek

Bloody Run Creek and the nearby seepages which run down the face of the Niagara Gorge were contaminated from the Hyde Park landfill. Prior to site remediation in 1994, the drainage from the Hyde Park landfill was a major source of dioxin contamination to the Niagara River (Gradient Corporation 1988). Bloody Run Creek passes through the Niagara gorge and discharges to the Niagara River at the base of the gorge (Appendix A3-Figure). Due to difficulties related to site access, this part of the creek and the bank of the Niagara River have not been remediated. There have been high concentrations of dioxins and furans in sediment and deployed mussels in this area.

In 2003, sediment collected from the shoreline (bank) of the Niagara River in the vicinity of Bloody Run Creek (in line with station 17) had extremely high concentrations of dioxins and furans (total TEQ; 121,922 pg/g (dioxin-like PCBs represent <1% of the total). Dioxin and furan concentrations in exposed sediment were lower in 2000 than in previous sediment surveys (TEQ of 3,732 pg/g) (Richman 2003). However, since the sediment along the shoreline had not been remediated, the 2000 data reflected the variability in local contamination rather than an improvement or decrease in sediment contamination. This was confirmed with the 2003 data and data collected from previous surveys. The 2003 results were similar to concentrations detected in 1993 (136,542 pg/g TEQ) and are

Figure 10: Dioxin and Furan Isomer Patterns in Sediment, 2003

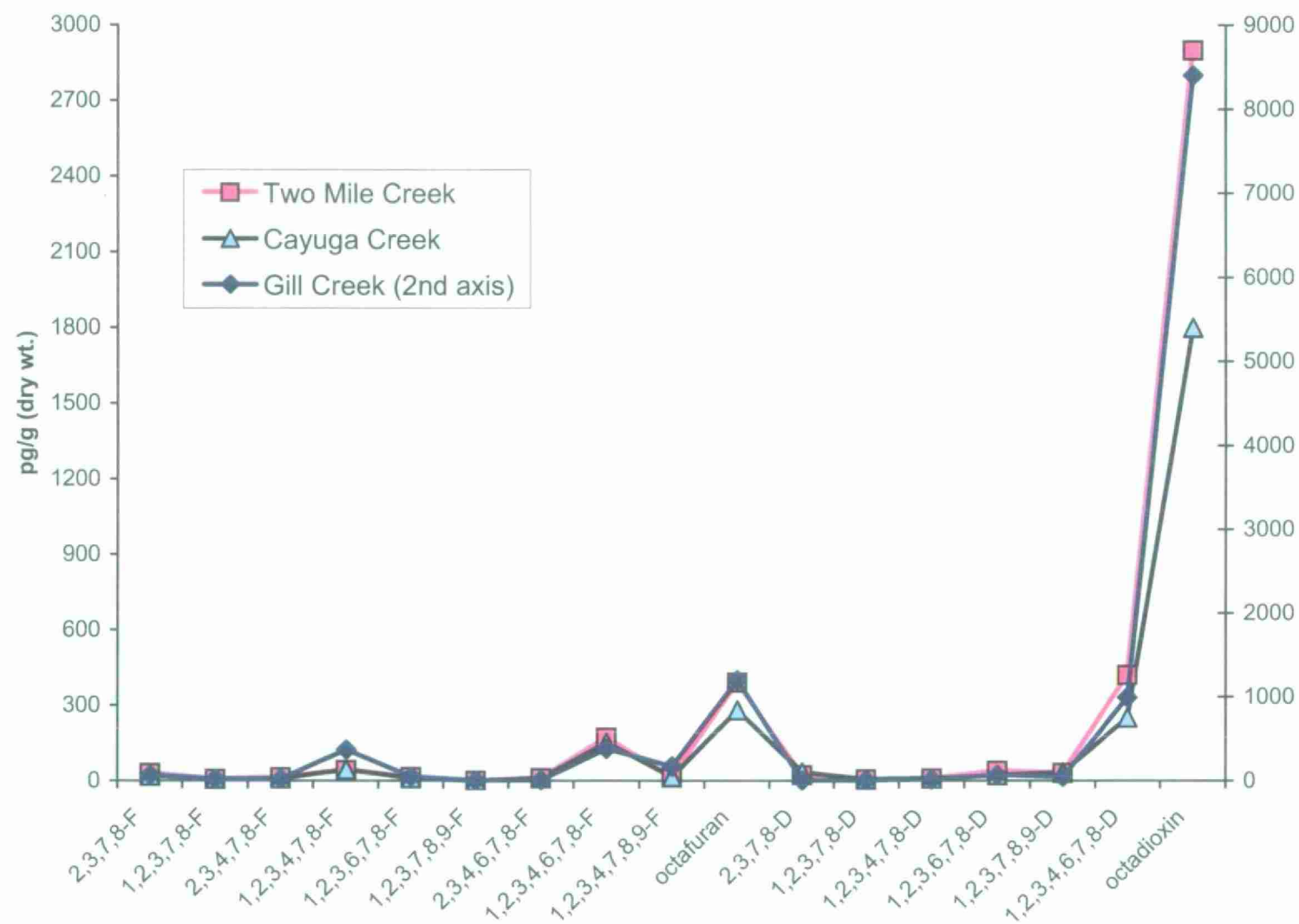
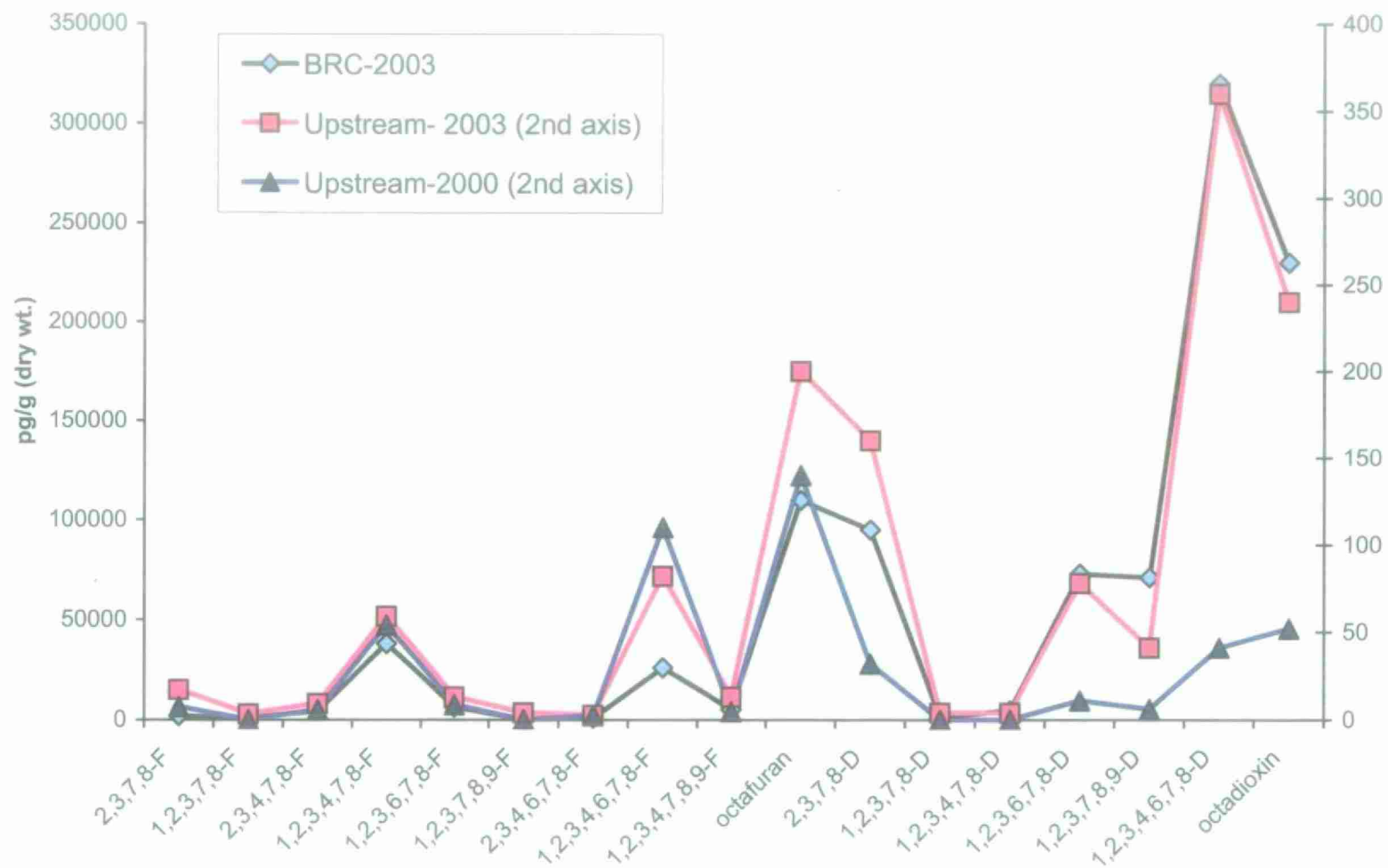


Figure 11: Dioxin and Furan Isomer Patterns in Sediment Collected Upstream of Bloody Run Creek and from the Mouth of the Creek



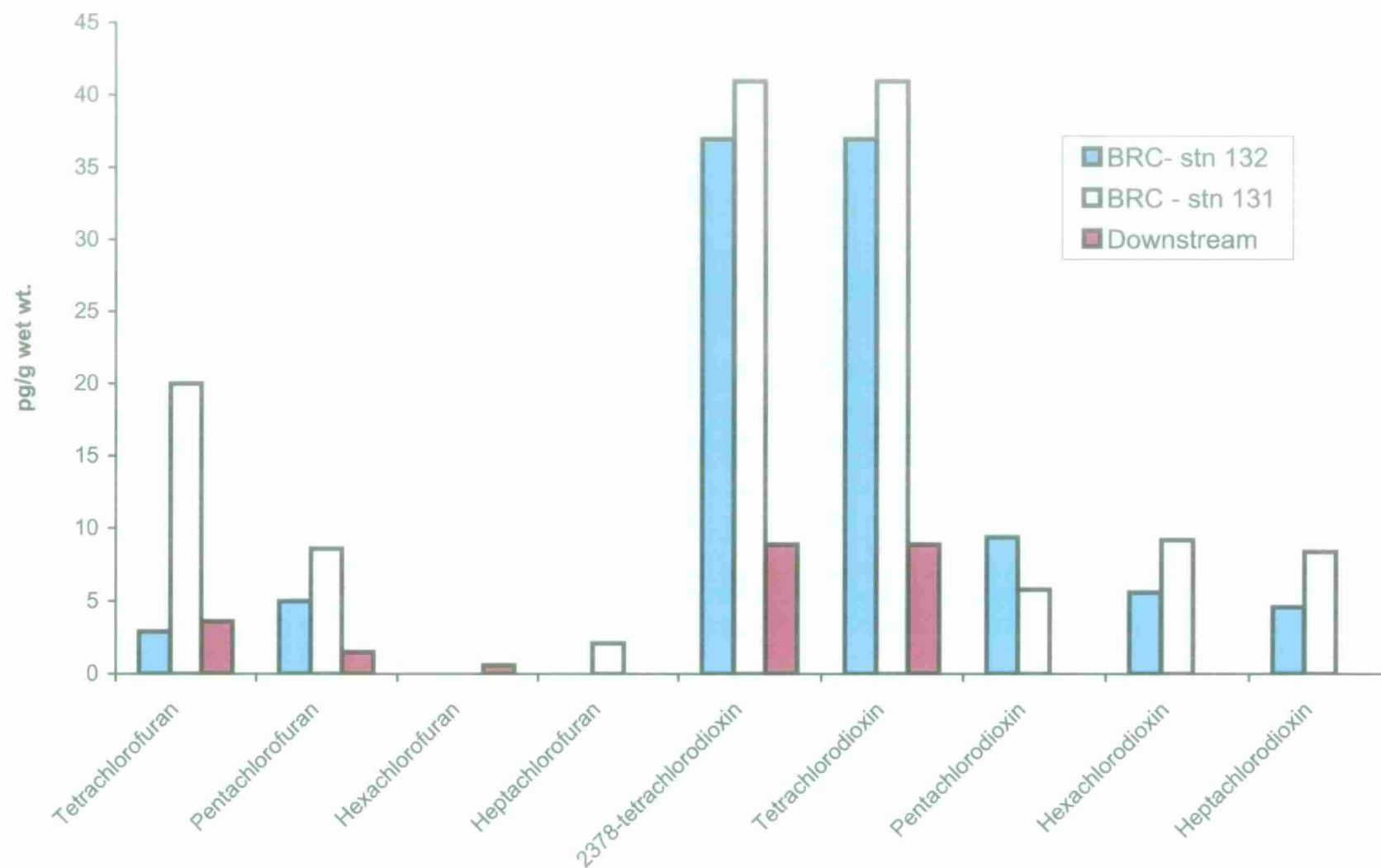
indicative of significant contamination. The selection of a site for the collection of sediment is highly variable between surveys and is dependant on the water level of the Niagara River at the time of sampling. As well, the rock slide in the gorge in 1994 altered the topography along the shoreline at the sampling station. Highly contaminated sediment was exposed in some spots due to the rock slide and buried in other locations.

Sediment was also collect from the Niagara River about 100 m upstream of the Bloody Run Creek sediment site and is referred to as the upstream station (station 18). In 2003 the total TEQ was 200 pg/g. This was higher than concentrations measured at this site in 2000 (50 pg/g) and suggested contamination of this sediment with dioxins and furans from Bloody Run Creek. The isomer patterns in this sediment sample were exactly the same as the pattern for the Bloody Run Creek site suggesting that a larger area of the shoreline may be contaminated than previously identified in these surveys (Figure 11). The pattern from 2000 resembled patterns in sediment collected from other stations upstream in the Niagara River (Figure 10 and 11) while the pattern from 2003 was more similar to the Bloody Run Creek signature which has a lower concentration of octadioxin relative to the 1,2,3,4,6,7,8-heptadioxin. As well, all the tetra-dioxin was in the form of 2,3,7,8-T4CDD (the most toxic form of dioxin). A review of the station positions (northing and easting) showed that the upstream sampling locations were different in 2000 and 2003. The 2003 site was about 44 m further upstream than the site in 2000 and about 27 m further offshore. Due to over hanging branches and dense vegetation it is difficult to obtain accurate GPS locations at this site. However, every attempt was made to resample similar locations.

Since the caged mussels were not retrieved from station 17 in 2003, this site was surveyed again in 2004 by deploying mussels at three locations along the shoreline. The total TEQ concentration in the mussel sample from upstream of Bloody Run Creek (station 18) was low at 0.3 pg/g and wholly due to the presence of dioxin-like PCBs (i.e. dioxins and furans were not detected) (Table 6a). The TEQ for the downstream station (station 25) was also low but showed some contamination relative to the upstream value (9.2 pg/g) which was due primarily to the presence of 2,3,7,8-T4CDD (Figure 12). In contrast to the upstream station, the contribution from dioxin-like PCBs to the total TEQ was only 3%. Of the three sites along the Niagara shoreline set up to monitor Bloody Run Creek (stations 130, 131 & 132), two had high TEQ concentrations (42 pg/g and 48 pg/g), almost exclusively due to the high concentrations of 2,3,7,8-T4CDD (> 98% of the total TEQ). The TEQ in the mussel sample collected from the third site, station 130, was low (representative of the dioxin-like PCBs). Although a value of 40 pg/g was reported for 2,3,7,8-TCDD (similar to the concentrations recorded for the other two samples), it was flagged as being below the detection limit due to analytical interference when the 2,3,7,8 TCDD isomer was analysed hence resulting in the low overall TEQ.

Total TEQs for mussels deployed at the site routinely used to monitor Bloody Run Creek (station 17) have ranged from as high as 278 pg/g in 1993 to 23 pg/g in 2000 with the median value of 85 pg/g in 1997. Station 17 is about 10 m further offshore than station 130. The variability in tissue concentrations in mussels between survey years could be due to the location of the cages relative to the creek mouth or the episodic nature of the runoff

Figure 12: Dioxin and Furan Congener Groups in Mussels Deployed Along the Shoreline Near the Mouth of Bloody Run Creek, 2004



from the site. Since the 1994 rock slide which buried the location of the mouth of the creek, the placement of the cages to capture runoff from the site has been problematic. In 2004, cages at station 131 and 132 were lined up with visible seeps from the area of the rock slide. The data from these two stations clearly showed that dioxins and furans were bioavailable from this site (as well as chlorinated benzenes) and were entering the Niagara River. Bloody Run Creek is still considered a source of dioxins and furans to the Niagara River and requires long term monitoring.

Pettit Flume

High concentrations of dioxins and furans were detected in mussels and sediment from the Pettit Flume inlet cove in 1997 suggesting that the area had been re-contaminated (Richman 1999) following the remediation in 1995. Accordingly, the contaminated sediment was removed in the spring of 2000 (US EPA and NYSDEC 2002). However, high concentrations of dioxins and furans were detected in deployed mussels and sediment collected in July 2000 and now again in 2003.

In 2003, sediment collected from the cove had a TEQ of 11,383 pg/g (less than 1% of the total TEQ is due to dioxin-like PCBs). This concentration is lower than concentrations reported in 1997 (20,073 pg/g) when the re-contamination of the cove was first identified, and lower than concentrations in 2000 (30,250 pg/g), however, these data still suggested extremely contaminated sediment. For comparison, sediment collected from the reference site located immediately upstream of the cove in the Little Niagara River (station 185) had a TEQ of 44 pg/g (Appendix A4-Figure). The total TEQ for caged mussels deployed in the cove was high at 66 pg/g, and comparable to the TEQ in 2000 (77 pg/g). Ninety-nine percent of the total was due to dioxin and furan contamination. Dioxins and furans were not present in the mussels deployed upstream of the Pettit Flume. The TEQ (0.04 pg/g) was due to the presence of dioxin-like PCBs present at low concentrations.

The high concentrations in mussel tissue suggested that these compounds were still bioavailable in this cove. Since fish, other aquatic biota and waterfowl move freely in and out of the cove to feed, the cove is a source of dioxins to indigenous biota.

High concentrations of dioxins and furans were also present in sediment collected from a station immediately downstream of the cove (TEQ: 2,078 pg/g), which suggested sediment transport from the cove. The concentration in 2003 was four times higher than in 2000 (502 pg/g TEQ) implicating the cove as a source of dioxins to the Niagara River. However, the TEQ for mussels deployed at this site was low (0.47 pg/g). The isomer patterns in the sediment collected from the cove and immediately downstream of the cove were consistent with previous samples from 1993 before remedial activities which suggested a common source (Figure 13 & 14). Patterns in sediment collected from the upstream station (station 185) do not match the patterns of the contaminated sediment but are similar to patterns detected in sediment collected from other sites in the Niagara River and the Erie Canal (Holiday Park site), which flows into the Little Niagara where station 185 is located (Figure 15).

Figure 13: Dioxin and Furan Isomer Patterns in Sediment, Pettit Flume (1993-2003)

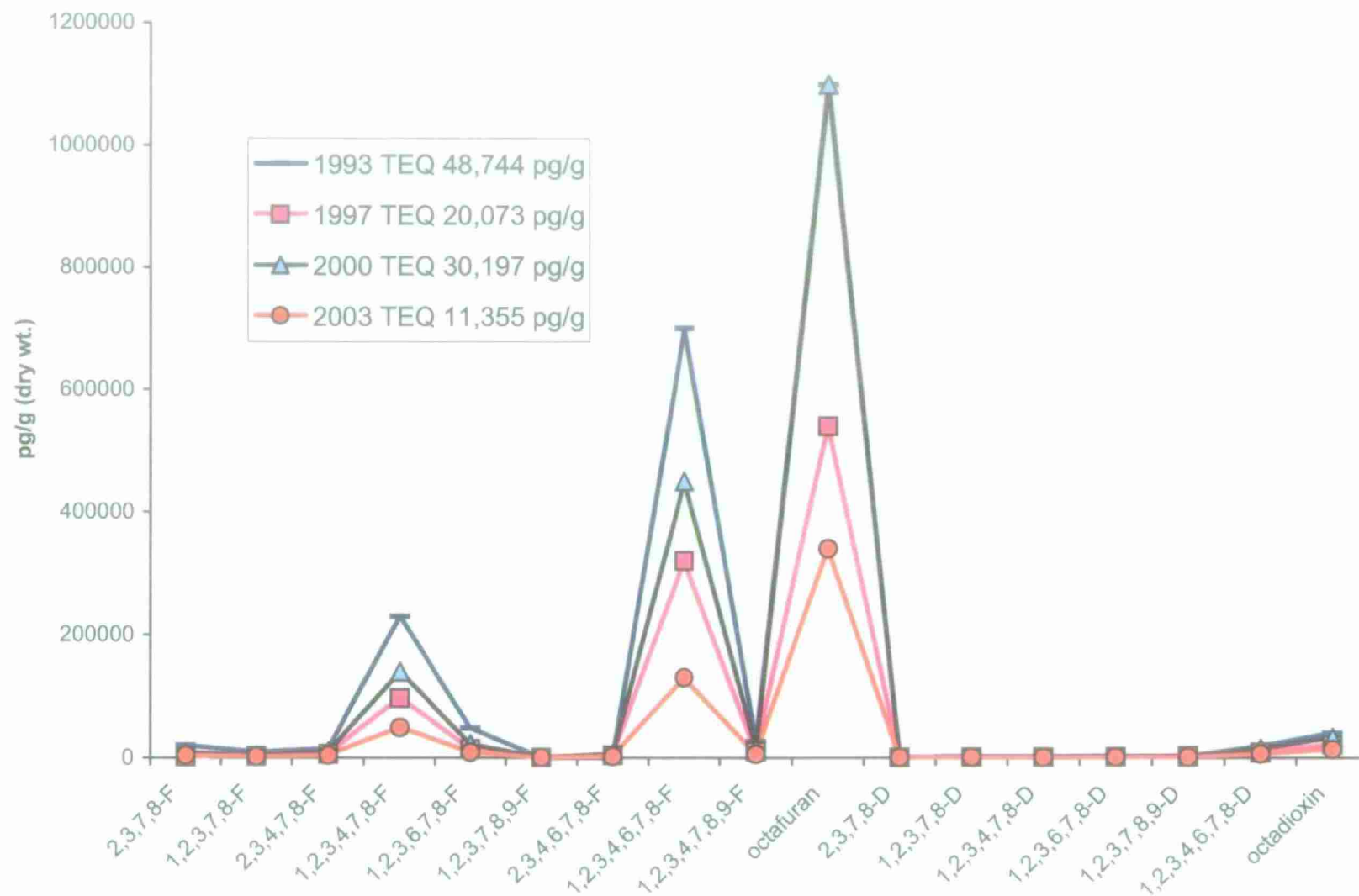


Figure 14: Dioxin and Furan Isomer Patterns in Sediment Collected Downstream of the Pettit Flume Cove

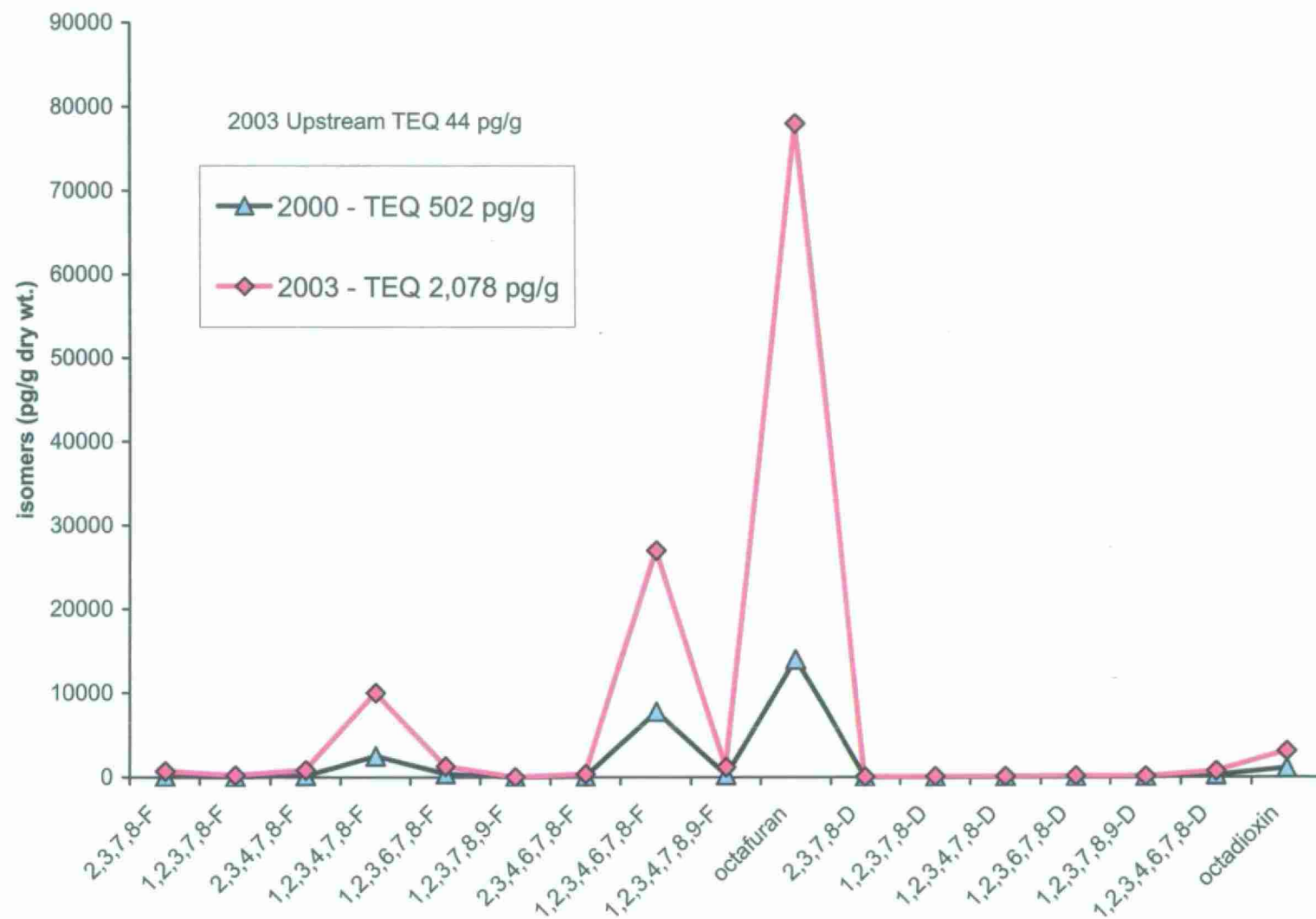
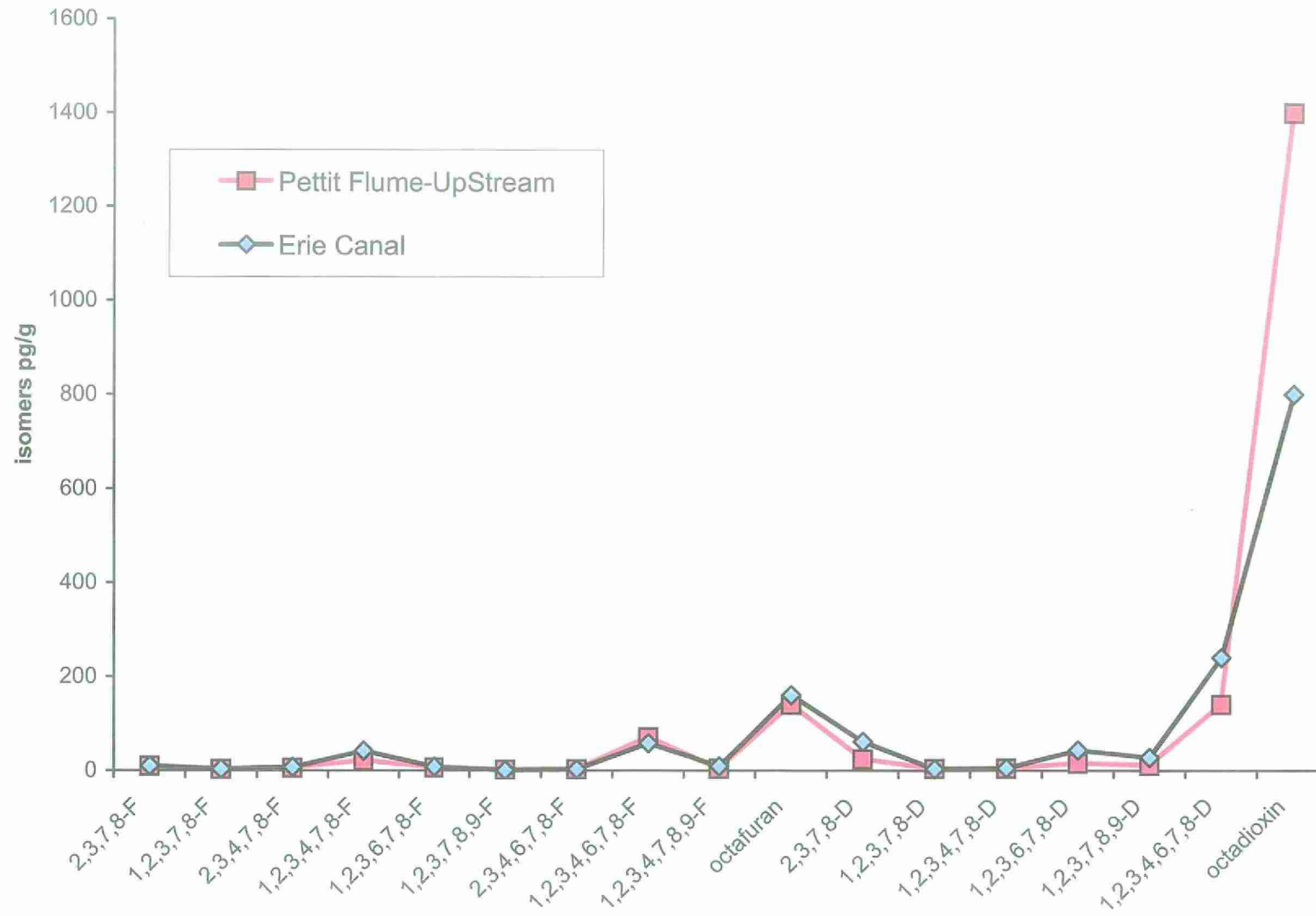


Figure 15: Dioxin and Furan Isomer Patterns in Sediment, 2003



Polybrominated Diphenyl Ethers (PBDEs)

Polybrominated diphenyl ethers were not listed as priority contaminants within the NRTMP but they have been identified as global pollutants and are present in all parts of the environment. Since PBDEs are an emerging environmental issue, they were included in the mussel monitoring survey. PBDEs are lipophilic, highly persistent in the environment and bioaccumulate (Palm *et al.* 2002; Tanabe 2004). Although concentrations in the environment are low, current levels may threaten some wildlife and invertebrates and may exert effects similar to those of PCBs, dioxins and furans (Tanabe 2004). There is concern about the presence of PBDEs since concentrations in the environment have been increasing since the 1970's (Palm *et al.* 2002; Hites 2004; Martin *et al.* 2004). This trend of increasing environmental concentrations has also been noted in the Niagara River by comparing concentrations of PBDEs in suspended sediments collected from the period 1980 to 2002 (Marvin *et al.* 2004). Accordingly, due to the recent analytical method development within the MOE laboratory, PBDEs have been included in the Niagara River mussel monitoring survey to assess their bioavailability in the river.

PBDEs were added to materials (vehicles, furniture, textiles, carpets, building materials, electronics, etc.) as flame retardants and easily volatilize into the atmosphere and enter the environment during the manufacturing and use of these products. They are a mixture of 209 individual congeners. The three most widely used mixtures are deca-BDE (97% pure deca), octa-BDE (blend of hepta and nona) and penta-BDE (blend of tetra to hexa) (deBoer and Cofino 2002).

PBDEs were detected in mussels deployed in the Niagara River (Table 8). Accordingly, caged *Elliptio complanata* was a useful bioindicator of PBDEs. The total concentration and congener patterns of PBDEs in the Balsam Lake control mussels (i.e. pre-deployment concentrations) suggested that PBDEs were also bioavailable in Balsam Lake. However, concentrations in the mussels were low (less than or close to the detection limit for most congeners), making it difficult to interpret the data (Figure 16). Possible sources could include the atmosphere and two sewage lagoons that discharge to the lake biannually. The total PBDE concentration (measured as the total sum of detectable individual PBDE congeners) in the Balsam Lake control mussels ranged from 0.28 to 1.0 ng/g (wet wt.). This range in concentrations overlapped with, or was greater than, concentrations detected in mussels deployed in the Chippawa Channel, Lyons Creek and Bloody Run Creek (Table 8). Accordingly, it was difficult to determine whether mussel PBDE concentrations at these stations were reflecting the pre-deployment concentrations or their deployment environment. Concentrations of BDE-47 and BDE-99, (typically detected at the highest concentrations in biota and in this study contributed from 64 to 82% of the total BDE concentration at the other stations), were both close to the detection limit in the mussels deployed in the Chippawa Channel, Lyons Creek and the Balsam Lake control mussels and contributed less than 42% of the total BDE concentration (Figure 17). Interestingly, for all but one mussel deployed at Balsam Lake, between 43% and 94% of the total BDE concentration was due to BDE-209. BDE-209 is typically not detected in biota due to its high log Kow (about 10) and low bioavailability and hence is generally associated with the

Table 8: Concentrations (ng/g wet wt.) of polybrominated diphenyl ethers in caged mussels, Niagara River, 2003.
All data were blank subtracted with the respective blank from each sample run prior to reporting.

Station Description	Field Number	% Lipid	BDE17	BDE28	BDE47	BDE49	BDE66	BDE71	BDE77	BDE85	BDE99	BDE100
Canadian Sites												
Chippawa Channel	GL045411		0.001	<	<	0.005	<	0.0009	<	0.0018	<	0.008
	GL045412		0.001	0.003	0.04	0.009	0.003	0.0005	<	0.003	0.008	0.018
	GL045413		<	<	<	0.004	0.001	0.0006	<	0.0028	0.008	0.008
Lyons Creek	GL045422		0.001	0.001	0.01	0.0057	0.0015	0.0007	<	0.0031	0.008	0.009
	GL045423	0.5	0.002	0.001	0.04	0.008	0.002	0.0006	<	0.0075	0.108	0.028
NOTL	GL045424		0.003	0.007	0.7	0.0273	0.012	0.0028	<	0.0575	0.909	0.178
	GL045425		0.002	0.002	0.23	0.0143	0.002	0.0017	<	0.0225	0.379	0.078
	GL045426		0.001	0.002	0.23	0.0163	0.004	0.002	<	0.0195	0.369	0.088
American Sites												
Buffalo River	GL045421		0.012	0.024	1.04	0.077	0.034	0.0084	0.0004	0.07	1.308	0.248
Tonawanda Channel (upstream Two Mile Creek)	GL045414		0.006	0.011	1.14	0.045	0.025	0.0048	1E-04	0.083	1.308	0.268
Two Mile Creek	GL045418		0.021	0.027	1.74	0.065	0.032	0.0082	0.0005	0.092	1.508	0.238
	GL045419	0.34	0.030	0.039	2.74	0.097	0.061	0.01	0.0005	0.128	2.408	0.418
	GL045420		0.028	0.011	2.34	0.092	0.019	0.011	<	0.118	2.008	0.358
102nd Street outfall	GL045427	0.78	0.004	0.007	0.55	0.0353	0.01	0.0027	<	0.0365	0.589	0.128
Cayuga Creek	GL035621	1.7	0.019	0.040	3.77	0.133	0.0728	0.0084	0.0001	0.097	2.88	0.511
Occidental - upstream of Sewer 003	GL035662	0.1	0.005	0.009	0.87	0.053	0.0308	0.0039	<	0.023	0.74	0.161
Occidental Sewer 003	GL035652	1.5	0.001	0.001	0.17	0.001	0.0118	0.0054	<	0.006	0.11	0.02
	GL035653	2.5	0.001	0.003	0.27	0.004	0.0128	<	<	0.0063	0.11	0.018
	GL035654	1.5	0.002	0.007	0.87	0.014	0.0218	0.0014	0.0001	0.017	0.32	0.071
Gill Creek - upstream within the creek	GL035606	1.8	0.045	0.062	3.27	0.243	0.0848	0.0154	<	0.093	2.38	0.481
Bloody Run Creek - upstream	GL043048	0.27	0.002	<	0.13	0.0088	<	0.0017	0.0003	0.007	0.09	0.017
Bloody Run Creek	GL043034	0.17	0.005	0.001	0.13	0.0088	0.0048	0.0017	0.0007	0.007	0.09	0.027
Bloody Run Creek	GL043027	0.46	0.003	0.003	0.03	0.0061	0.0008	0.0003	0.0003	0.005	0.09	0.017
Bloody Run Creek	GL043020	0.45	0.004	0.003	0.03	0.0057	0.0038	0.0003	<	0.005	0.09	0.027
Bloody Run Creek - downstream	GL043013	0.34	0.004	0.005	0.03	0.0052	<	0.0001	0.0006	0.007	0.09	0.017
Balsam Lake Control	GL045428		0.002	0.003	0.03	0.0103	<	0.001	<	0.0095	0.139	0.042
	GL045429	0.27	<	0.001	0.03	0.0053	<	<	<	0.0055	0.029	0.008
	GL045430		<	<	<	0.0053	0.196	<	<	<	<	<
Balsam Lake Control	GL043006	0.32	0.003	0.008	0.13	0.0098	0.0058	0.0006	0.0007	0.012	0.2	0.027

average blank ± Standard Deviation (n=4)

0.002±0.002 0.004±0.005 0.23±0.13 0.007±0.007 0.004±0.001 0.001±0.001 0.001±0.001 0.003±0.001 0.098±0.022 0.027±0.008

"<" Compound was below the detection limit

Table 8: Concentrations (ng/g wet wt.) of polybrominated diphenyl ethers in caged mussels, Niagara River, 2003.
All data were blank subtracted with the respective blank from each sample run prior to reporting.

Station Description	BDE119	BDE126	BDE138	BDE153	BDE154	BDE183	BDE209	Total PBDE ng/g wet wt.	Total PBDE lipid normalized
Canadian Sites									
Chippawa Channel	<	<	<	0.0115	0.011	0.0094	0.138	0.19	
	0.001	<	0.002	0.0125	0.014	0.0044	0.138	0.26	
	<	<	<	0.0125	0.009	0.0134	0.868	0.93	
Lyons Creek	<	<	<	0.0105	0.008	0.0164	0.238	0.31	
	<	<	<	0.0185	0.014	0.0049	0.178	0.41	83
NOTL	0.0004	<	0.0002	0.0914	0.0933	0.0049	0.405	2.49	
	<	<	0.0002	0.0424	0.0493	0.0047	0.105	0.93	
	0.0004	<	0.0012	0.0434	0.0483	0.0009	0.105	0.93	
American Sites									
Buffalo River	0.003	0.001	0.0035	0.1065	0.126	0.006	0.138	3.21	
Tonawanda Channel (upstream Two Mile Creek)	0.001	0.001	0.0062	0.1265	0.126	0.005	0.138	3.29	
Two Mile Creek	0.001	<	0.0042	0.0965	0.082	0.0074	0.038	3.96	
	0.003	0.001	0.006	0.1565	0.146	0.0036	0.038	6.29	1849
	0.001	0.002	0.0076	0.1365	0.126	0.0104	0.018	5.29	
102nd Street outfall	<	0.0007	0.0052	0.0684	0.0723	0.0043	0.135	1.65	211
Cayuga Creek	0.0009	<	0.0021	0.278	0.225	0.0073	0.527	8.57	504
Occidental - upstream of Sewer 003	0.0009	0.0004	0.0011	0.08	0.085	0.0013	0.207	2.27	2271
Occidental Sewer 003	<	<	1E-04	0.017	0.009	0.0013	0.187	0.54	36
	<	<	1E-04	<	0.185	<	0.147	0.76	30
	0.0029	0.0004	<	0.028	0.013	0.0003	0.157	1.53	102
Gill Creek - upstream within the creek	0.0019	0.0004	<	0.188	0.195	0.0033	0.167	7.23	402
Bloody Run Creek - upstream	<	0.0004	<	0.02	0.0193	0.0021	<	0.30	110
Bloody Run Creek	0.0002	0.0004	0.001	0.022	0.0253	0.0021	<	0.33	192
Bloody Run Creek	0.0005	0.0002	0.003	0.016	0.0133	0.0021	<	0.19	41
Bloody Run Creek	0.0005	0.0004	0.003	0.028	0.0273	0.0022	<	0.23	51
Bloody Run Creek - downstream	0.0005	0.0014	0.002	0.018	0.0223	0.002	<	0.21	60
Balsam Lake Control	0.0014	0.0017	0.0052	0.0314	0.0503	0.0029	0.005	0.33	
	<	<	0.0012	0.0074	0.0153	0.0019	0.175	0.28	104
	<	<	<	0.0024	0.0063	<	0.645	0.86	
Balsam Lake Control	0.0015	0.0004	0.001	0.036	0.0273	0.0021	0.53	1.00	311

average blank ± Standard Deviation (n=4)

0.001±0.001 0.001±0.001 0.003±0.003 0.006±0.004 0.007±0.006 0.002±0.001 0.17±0.20

"<" Compound was below the detection limit

Figure 16: PBDE Congener Patterns in Replicate Balsam Lake Control Mussels

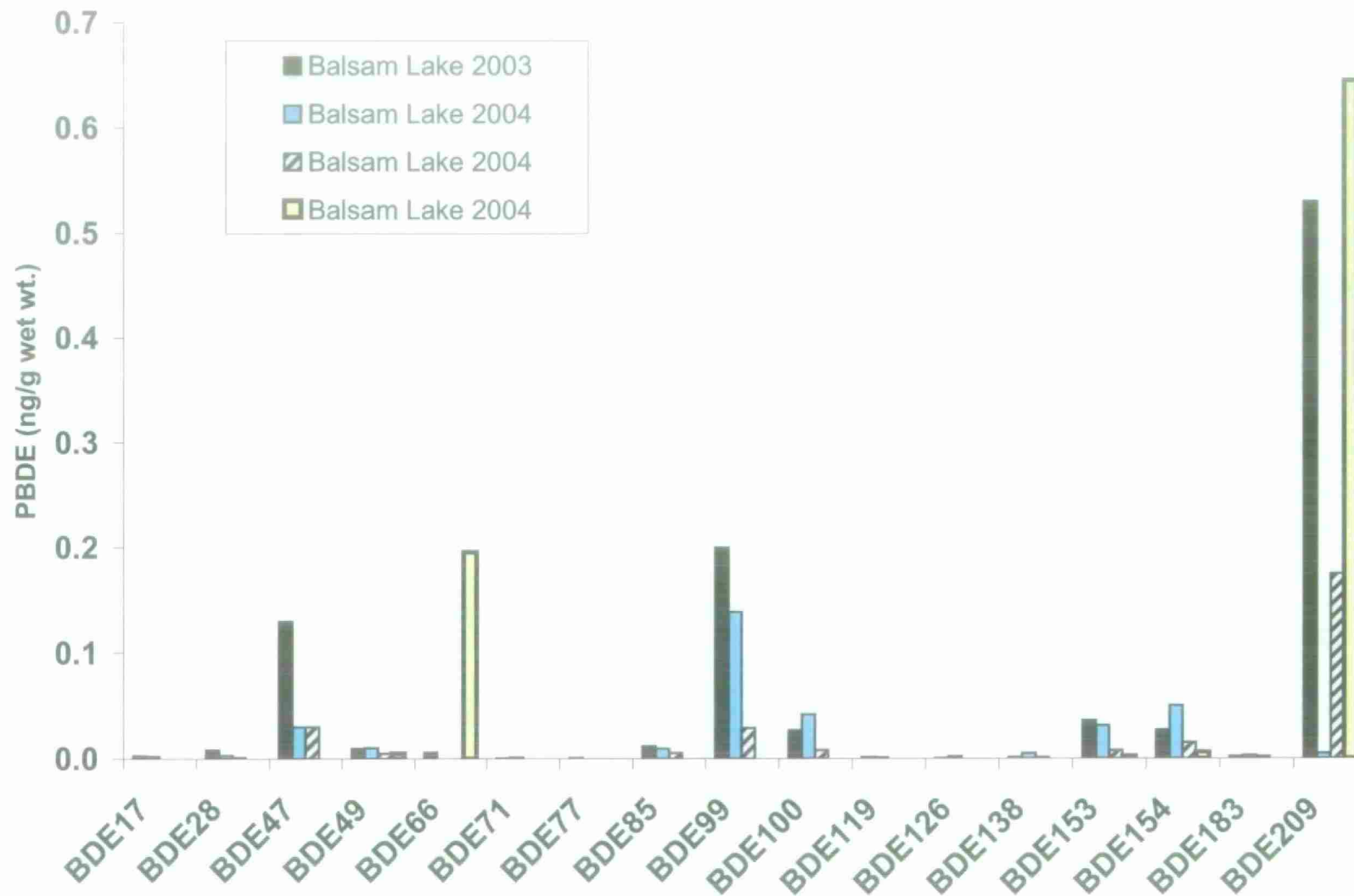
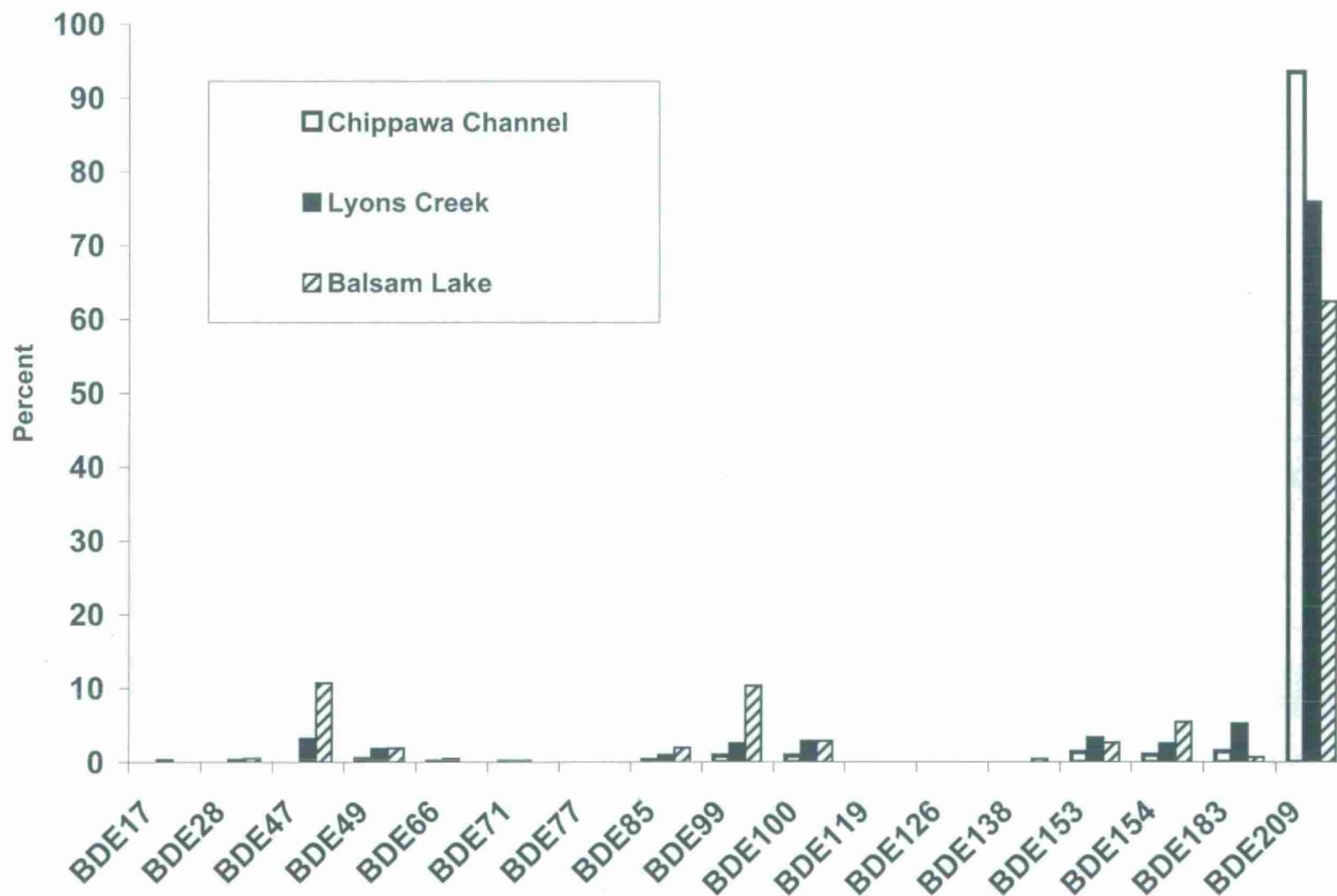


Figure 17: Percent Contribution of Individual Congeners to Total PBDE Concentration in Mussel Tissue (n=1)



sediment (Christensen and Platz, 2001; Eljarrat et al., 2005). The presence of BDE-209 in most of the mussel samples in the survey could be a reflection of suspended particulate matter since mussels were not depurated prior to processing their tissue. The low concentrations of the other congeners could be reflecting the low bioavailability of BDEs in these locations.

The highest concentrations in the survey were present in mussels deployed within tributaries to the American side of the Niagara River (Cayuga Creek - 8.6 ng/g; Gill Creek - 7.2 ng/g; and Two Mile Creek - range 4.0 to 6.3 ng/g). In addition to contributions from the atmosphere (which should be fairly consistent among all sites within the survey), each of these tributaries have storm sewers, hazardous waste sites, landfills and industries located nearby the sampling sites that could be potential sources of PBDEs. Total PBDE concentrations were also higher in mussels deployed at all sites in the Tonawanda Channel and Buffalo River (range: 1.7 to 3.3 ng/g) compared with mussels deployed on the Canadian side (Chippawa Channel) and in the lower Niagara (Bloody Run Creek and NOTL). This could be a reflection of the relatively higher degree of industrial activity and larger urban centres within the Tonawanda Channel compared with the other areas.

Typically, the most common congeners detected in freshwater and marine fish, birds and mammals have been BDE-47, followed by BDE-99 and BDE-100 (Christensen *et al.* 2002; de Boer *et al.* 2003; Zennegg *et al.* 2003; Martin *et al.* 2004; Oros *et al.* 2005). Penta-BDEs (e.g. BDE-47) and tetra-BDEs (e.g. BDE-99, BDE-100) are believed to be the most biologically active and most hazardous congeners. Since they are found in biota, sediments and sewage sludge they are likely persistent in the environment. Studies using caged and native mussels have also reported the detection of these three congeners which are suggestive of the penta-BDE formulation as a source (Christensen *et al.* 2002; Palm *et al.* 2002; Bayen *et al.* 2003; de Boer *et al.* 2003; Oros *et al.* 2005). This formulation is mostly used in North America and was the most common pattern found in the mussels deployed in the Niagara River and tributaries. Although concentrations in mussels deployed along the US side of the upper Niagara River were lower than for mussels deployed in the tributaries, the PBDE congener patterns were similar among the mussels, with BDE-47, -99 and -100 representing the highest concentrations relative to the other detectable congeners (Figure 18). Generally, at the stations in the tributaries, BDE-47 contributed a greater percentage to the total concentration than BDE-99, while for stations in the Buffalo River and Tonawanda Channel BDE-99 contributed a greater percentage to the total concentration than BDE-47 (Figure 19). However, overall, within a sampling site, actual concentrations of these two congeners were fairly similar in deployed mussels and combined, they contributed between 64 to 82% of the total BDE concentration. For mussels at the stations associated with the Occidental facility the difference in concentrations between the two congeners was greater than for the other stations with BDE-47 contributing 31 to 57% of the total and BDE-99 only 15 to 21% of the total BDE concentration. This shift in congener patterns could represent exposure to a different composition of the commercial penta-BDE mixtures. For example, Bayen *et al.* 2003 described one commercial mixture, DE-71 as having a composition of 47% BDE-99 and 25% BDE-47 while Bromkal 70-5DE has a composition of 35 and 37% of BDE-99 and -47

Figure 18: Polybrominated Diphenyl Ethers in caged Mussels, Niagara River, 2003 (n=1)

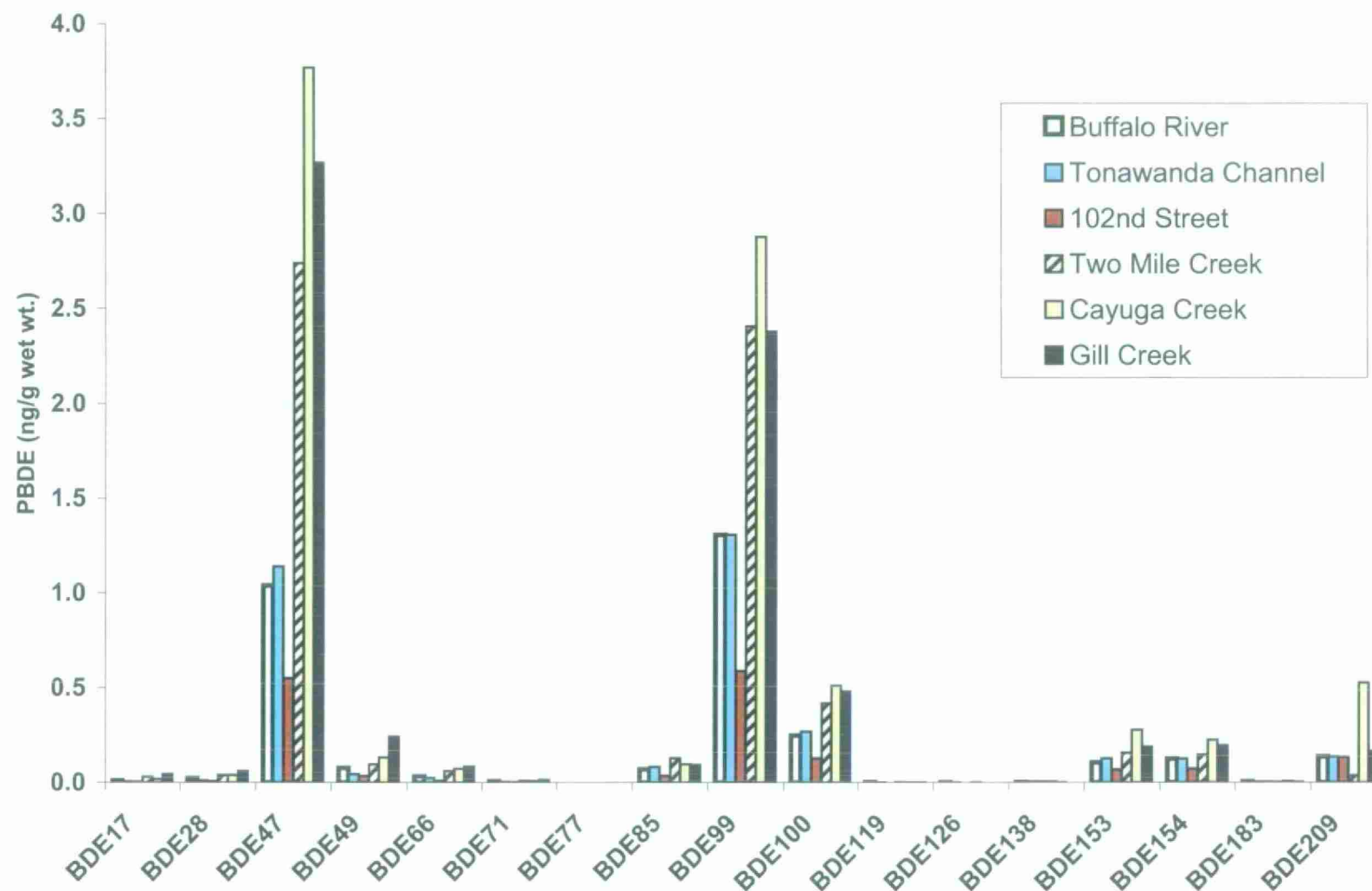
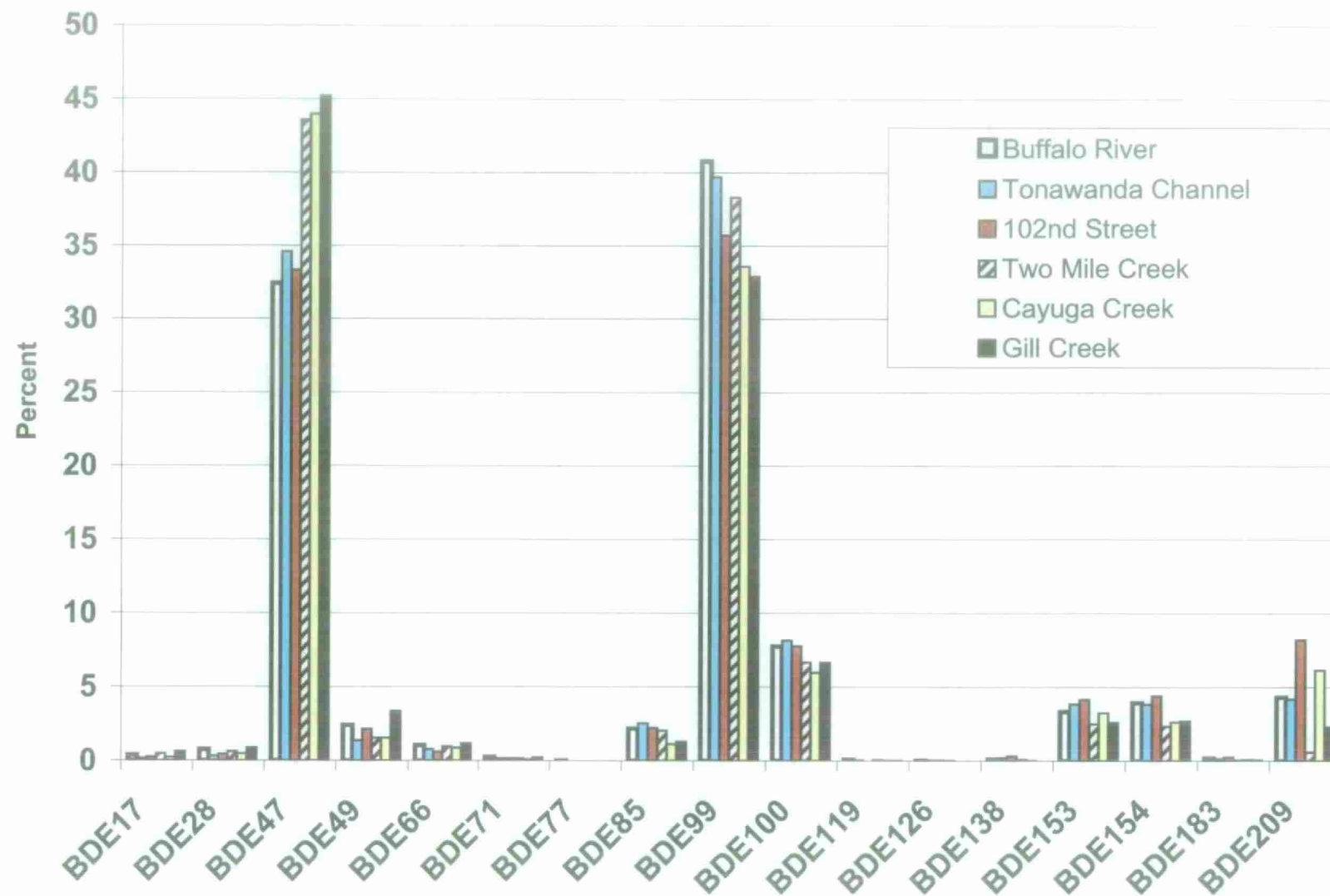


Figure 19: Percent Contribution of Individual Congeners to Total PBDE Concentration in Mussel Tissue (n=1)



respectively. However, according to Hites (2004), the use of congener patterns to identify particular PBDE sources is difficult. In addition to different commercial mixture being discharged into the environment, congener patterns in the air, water, sediment and different levels of the food chain are influenced by the differences in bioavailability, bioaccumulation and biodegradation of the individual congeners.

To determine the relative bioavailability of PBDEs in the Niagara River, comparisons were made with other studies where bivalve concentrations were measured. The total concentration of PBDEs in the caged mussels deployed in the tributaries were consistent with data collected from other studies in industrialized areas. Bayen *et al.* (2003), reported PBDEs in green mussels in the coastal waters of Singapore with concentrations ranging from 0.29 to 8.6 ng/g wet wt. PBDE-47, -99, -100 and -153 were also the dominant congeners. These mussels were collected from an industrialized area where there were several electronic manufacturing and electronic waste-recycling companies. Caged San Francisco Estuary mussels (*Mytilus californianus*) deployed for 90 days had concentrations which ranged from 1.3 to 3.7 ng/g wet wt. (sum of BDE-47, -99, -100) (Oros *et al.* 2005). Likely sources to the Estuary were local wastewater treatment plants and washout and emissions from a refuse dump. These values were similar to concentrations measured in the mussels deployed in the upper Niagara River. However, clams that were resident in the Estuary, had concentrations that were two to three times higher than concentrations detected in the deployed mussels. Presently, data for mussels resident to the Niagara River (e.g. quagga mussels) are unavailable. The caged mussels in the US tributaries had higher concentrations than mussels collected from reference and industrial areas in the Netherlands (blue mussels < 2 ng/g), Denmark (blue mussels range from 0.08 to 0.81 ng/g) and compared with mussels from a reference area in Greenland (blue mussels < 0.11 ng/g).

Within station variability for individual congeners was reviewed at stations where there were replicate mussels analysed (e.g. Chippawa Channel, NOTL, Two Mile Creek, Occidental Sewer 003). For the most commonly detected congeners (-47, -99, -100, -153, -154) replicate mussels showed the least variability in Two Mile Creek since this station had concentrations well above the detection limits and blank data (coefficients of variation (CV) ranged from 22 to 28%). However, variability between replicates was higher at the remaining stations since concentrations in the mussel tissue were low for most of the congeners and at times only detected in one or two of the three mussels analysed. Since there is currently limited data on PBDEs in deployed biomonitors, future studies will include at least five replicate samples within a station or composite samples to better account for within station variability.

SUMMARY OF SIGNIFICANT FINDINGS AND RECOMMENDATIONS

- 1) p,p'-DDE was detected in mussels at a few stations on both sides of the river at low concentrations indicating that historic contamination with this compound is persistent and widespread. The highest concentrations were present in mussels deployed in Lyons Creek. HCH was detected at two sites on the U.S. side of the river at concentrations previously detected in other Niagara River mussel surveys. Concentrations are typically low.
- 2) High concentrations of total PCBs were detected in mussels deployed in Lyons Creek on the Canadian side of the river. Remedial actions in Lyons Creek are presently being investigated and are pending the completion of an environmental risk assessment.
- 3) Trace concentrations of total PCBs were detected at almost all stations on the American side of the river and in the Chippawa Channel suggesting that PCB exposure was pervasive in the Niagara River in general, and that PCBs will likely be bioavailable at low concentrations in the future, similar to the continued bioavailability of DDT and its metabolites. With the exception of mussels deployed in Lyon's Creek, concentrations of total PCBs in mussels were low.
- 4) High concentrations of total PCBs were detected in sediment collected from the mouth of Gill Creek, Bloody Run Creek and the Occidental Sewer 003 outfall. The presence of PCB in sediment at these sites is likely due to historic contamination.
- 5) In general, the most frequently detected chlorinated benzenes in the survey were: hexachlorobenzene (HCB), hexachlorobutadiene (HCBd), 1,2,3,5-tetrachlorobenzene and 2,3,6-trichlorotoluene. Concentrations of these parameters in mussels were typical of those observed in previous mussel monitoring surveys.
- 6) Concentrations of chlorinated benzenes and chlorotoluene in mussels deployed at the Occidental Sewer 003 site were relatively low in 1997, 2000 and 2003 compared with data collected between 1983 and 1995. However, data for HCBd have been consistent since 1993 and concentrations were high relative to other sites monitored in the surveys with the exception of Gill Creek. This suggests that HCBd may be present in the effluent from this outfall.
- 7) PAHs were detected in caged mussels. The highest concentrations were at sites associated with storm sewers and urban creeks (e.g. Cayuga Creek, Two Mile Creek, Pettit Flume, mouth of the storm sewer discharging to the Niagara River downstream of Superior Lubricant). PAH compounds having both the highest concentrations and detected most frequently were benzo(b)fluoranthene, chrysene, flouranthene, and pyrene. Control of PAHs would be difficult given that the atmosphere and surface runoff may be important sources.

- 8) High concentrations of dioxins and furans continue to be detected in mussels and sediment from the Pettit Flume inlet cove. The source of the dioxins and furans remains unclear given the extensive remedial activities at this site. The TEQ for the Pettit Flume cove sediment was 11,383 pg/g and for mussels 66 pg/g. Dioxin-like PCBs contribute less than 1% to the total TEQ. The source of the re-contamination of this cove requires further investigation and control, particularly since the sediment immediately downstream of the cove were also contaminated. Concentrations were at least four times higher than in 2000 which suggests that contaminated sediment continues to migrate out of the cove. Continued monitoring of this site is still recommended for future surveys.
- 9) Dioxin and furan concentrations in sediment from the Niagara River shoreline at the Bloody Run Creek site were high 121,725 pg/g and similar to concentrations detected in 1993 (136,542 pg/g TEQ) and are indicative of significant contamination. Concentrations of dioxins and furans in mussels deployed in 2004 ranged as high as 48 pg/g. 2,3,7,8-TCDD represents 98% of the total tetra chlorinated dioxin present in sediment and mussels samples and at least 78% of the total TEQ. Concentrations of several chlorinated benzene compounds were also high relative to the upstream reference site and other sites monitored in the Niagara River. The data indicate that this site is still contaminated with these parameters and continues to act as a source to the Niagara River. Continued monitoring of this site is still recommended for future surveys.
- 10) Sediment collected from Gill Creek upstream of the creek mouth was contaminated with dioxins and furans (119 pg/g TEQ). Given the recent remediation (dredging in 1998) of sediment in Gill Creek the data suggested that there may be a source that requires further investigation. However, the bioavailability of the dioxins and furans may be low given the low TEQ concentration in deployed mussels (0.58 pg/g).
- 12) Polybrominated diphenyl ethers were detected in mussels deployed in the Niagara River. Caged *Elliptio complanata* was a useful bioindicator of this highly persistent global pollutant. However, at least five replicate mussels should be deployed within a selected number of stations to better assess the variability in concentrations between mussels. Composite samples should be used at the remaining stations. The highest concentrations (measured as the total sum of detectable individual PBDE congeners) were present in mussels deployed within tributaries to the American side of the Niagara River (Cayuga Creek - 8.6 ng/g wet wt.; Gill Creek - 7.2 ng/g; and Two Mile Creek - range 4.0 to 6.3 ng/g).

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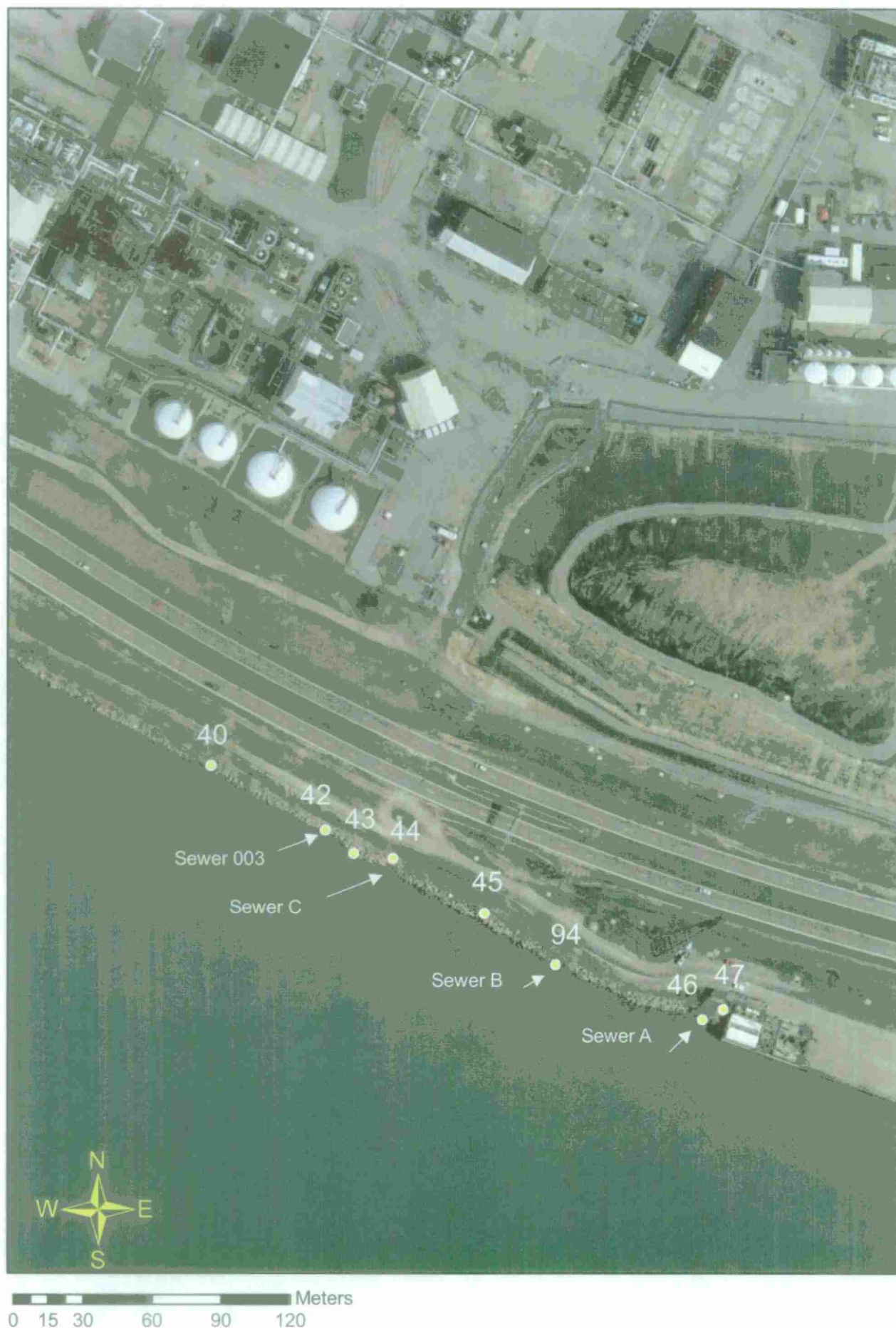
APPENDICES

Appendix A: Station location (northing/easting), water temperature, conductivity and dissolved oxygen at stations measured during deployment and retrieval, 2003

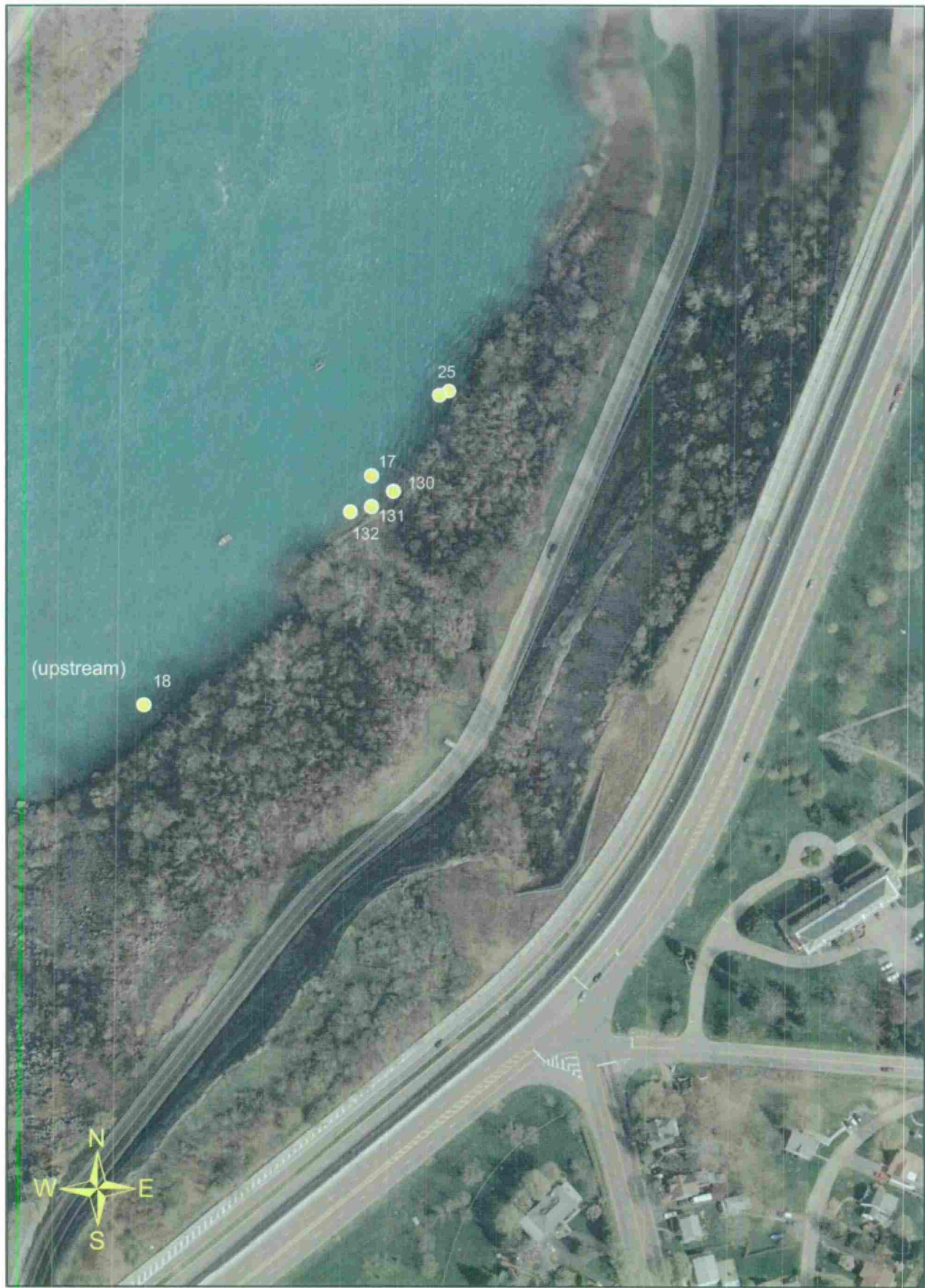
Station name	Station #	Northing [mN]	Easting [mE]	Accuracy [m]	TEMP [°C]	D.O. [mg/L]	COND [mmhos]	TEMP [°C]	D.O. [mg/L]	COND [mmhos]
						Deployment			Recovery	
Upstream Gill Creek	05-15-0022	4772073	660856	n/o	22.0	4.6	528	23.9	3.4	481
Gill Creek @ mouth (US of outfall)	05-02-0037	4771400	660691	7	21.7	7.6	291	23.4	8.3	300
Gill Creek @ mouth (DS of outfall)	05-02-0037	4771394	660673	n/o	22.2	7.5	277	23.8	9.3	230
Cayuga Creek	05-15-0031	4771991	665963	8	20.6	3.2	1033	22.3	3.7	813
102 nd Street	05-02-0022	4770962	666801	3	22.6	9.0	282	Mussel Lost		
102 nd Street Upstream site	05-02-0093	4770772	667260	7	22.6	9.6	270	25.7	9.8	309
102 nd Street- new Upstream site @ storm sewer	05-05-0023	4770806	667258	7	18.5	5.0	768	24.3	8.3	430
Downstream Gratwick Riverside Park	05-02-0199	4769281	670599	n/o	22.6	8.8	263	25.0	9.1	282
Upstream Gratwick Riverside Park	05-02-0031	4768289	671662	n/o	22.2	7.4	279	Meter Inoperative		
Sotrm sewer - Downstream of Superior Lubricant	05-02-0004	4768613	671370	n/o	22.7	9.1	268	24.0		322
Upstream Bloody Run Creek	11-02-0018	4777862	659070	15	21.4	9.2	266	23.3	9.9	270
Bloody Run Creek	11-02-0017	4777968	659161	7	21.4	9.6	265	Mussel Lost		
Downstream Bloody Run Creek	11-02-0025	4778007	659192	13	21.5	10.1	265	23.4	9.0	269
Downstream Sewer 003	05-02-0040	4771095	662175	5	22.1	7.0	269	23.9	7.9	310
Occidental's Sewer 003	05-02-0042	4771071	662226	5	23.1	7.7	302	Meter Inoperative		
Downstream of Storm Sewer (C)	05-02-0043	4771062	662239	7	22.2	7.2	281	24.2	8.9	291
Storm Sewer (C) Occidental Facility	05-02-0044	4771061	662256	4	22.2	7.7	269	24.4	8.8	292
Between Storm Sewer (C) and Storm Sewer (B)	05-02-0045	4771040	662297	5	22.1	7.6	266	24.4	8.9	292
Storm Sewer (B), Occidental Facility	05-02-0094	4771020	662329	4	22.2	7.4	267	24.3	8.8	293
Storm Sewer (A), Occidental Facility	05-02-0046	4771001	662394	n/o	22.2	7.8	267	24.4	9.4	294
Upstream of Storm Sewer (A)	05-02-0047	4771008	662410	6	22.2	7.6	266	24.4	9.4	294
Pettit Flume (Upstream)	05-02-0185	4766730	672249	6	28 *	7 *	200 *	24.5	8.5	283
Pettit Flume (Site B)	05-02-0186	4766811	672243	6	22.7	6.9	390	23.3	9.1	289
Pettit Flume (Downstream)	05-02-0187	4766797	672175	6	26.3	7.0	218	24.6	9.4	280
Upstream Exolon	05-15-0033	4765160	675036	7	23.1	7.4	298	24.5	6.9	369
Downstream Exolon	05-15-0034	4765489	674574	9	23.1	7.5	283	25.2	8.4	365
Two Mile Creek	05-02-0197	4764036	670594	13	26.0	6.6	823	23.2	5.7	838
Tonwanda Channel Upstream Two Mle Creek	05-02-0092	4763887	670066	6	22.6	7.8	260	24.8	8.6	277
Buffalo River	05-02-0220	4748091	674096	12	23.7	3.5	450	27.3	7.5	452
Fort Erie at Robertson St.	05-02-0203	4754947	670284	6	22.3	9.3	263	25.6	7.8	263
Lyons Creek	05-15-0020	4759547	645135	3	22.0	8.5	250	23.7	7.8	274
Frenchmans Creek at Durez	05-15-0019	4755213	668298	6	19.2	6.6	918	21.1	7.9	657
Chippawa Channel	05-02-0051	4768219	661222	5	21.7	7.9	272	23.3	8.5	278
Niagara-on-the-Lake	11-02-0009	4790830	657458	7	21.9	9.0	263	24.5	8.9	268
Upstream Bloody Run Creek-2004	11-02-0018	4777632	659024					22.0	9.0	265
Bloody Run Creek-2004	11-02-0130	4777962	659171					21.8	9.5	277
Bloody Run Creek-2004	11-02-0131	4777955	659162					21.1	8.6	267
Bloody Run Creek-2004	11-02-0132	4777952	659153					22.1	9.3	267
Downstream Bloody Run Creek-2004	11-02-0025	4778005	659188					22.2	8.4	265

* New batteries in meter, probable insufficient warmup time

Appendix A2: Sampling Stations at the Occidental Chemical Company.
Niagara River, 2003.



Appendix A3: Sampling Stations at Bloody Run Creek,
Niagara River, 2003 & 2004



0 20 40 80 120 160 Meters

Appendix A4: Sampling Stations at the Pettit Flume Cove,
Niagara River, 2003



Appendix B: Mussel tissue wet weight (g). Niagara River, 2003

Station Name	Station Number	Sample Number	Sample Weight Wet [g]	Comment
Upstream Gill Creek	05-15-0022	35603	7.5	1 mussel
		35604	7.5	1 mussel
		35605	8.9	1 mussel
		35606	7.3	1 mussel
		35607	31.4	4 mussel composite
Gill Creek @ mouth (US of outfall)	05-02-0037	35611	8.9	1 mussel
		35612	6.9	1 mussel
		35613	6.2	1 mussel
Gill Creek @ mouth (DS of outfall)	05-02-0037	35614	7.3	1 mussel
		35615	6.0	1 mussel
		35616	8.7	1 mussel
Cayuga Creek	05-15-0031	35617	9.4	1 mussel
		35618	7.1	1 mussel
		35619	7.1	1 mussel
		35620	36.0	4 mussel composite
		35621	8.1	1 mussel
Storm sewer - Downstream of Superior Lubricant	05-02-0004	35622	8.3	1 mussel
		35623	8.5	1 mussel
		35624	8.5	1 mussel
Upstream Gratwick Riverside Park	05-02-0031	35625	8.7	1 mussel
		35626	7.0	1 mussel
		35627	6.5	1 mussel
Downstream Gratwick Riverside Park	05-02-0199	35628	6.1	1 mussel
		35629	5.3	1 mussel
		35630	7.6	1 mussel
102 nd Street Upstream site	05-02-0093	35634	9.5	1 mussel
		35635	9.5	1 mussel
		35636	9.5	1 mussel
102 nd Street- new Upstream site @ storm sewer	05-	35637	8.4	1 mussel
		35638	8.3	1 mussel
		35639	6.8	1 mussel
Downstream Bloody Run Creek	11-02-0025	35640	6.0	1 mussel
		35641	5.9	1 mussel
		35642	5.7	1 mussel
Upstream Bloody Run Creek	11-02-0018	35643	6.7	1 mussel
		35644	7.0	1 mussel
		35645	7.3	1 mussel
Downstream Sewer 003	05-02-0040	35646	6.4	1 mussel
		35647	6.6	1 mussel
		35648	7.9	1 mussel
Occidental's Sewer 003	05-02-0042	35649	7.3	1 mussel
		35650	5.5	1 mussel
		35651	8.0	1 mussel
		35652	6.9	1 mussel
		35653	5.4	1 mussel

Appendix B: Mussel tissue wet weight (g). Niagara River, 2003

		35654	6.6	1 mussel
Downstream of Storm Sewer (C)	05-02-0043	35661	28.1	4 mussel composite
		35662	5.3	1 mussel
		35663	5.2	1 mussel
		35664	8.0	1 mussel
		35665	6.7	1 mussel
Storm Sewer (C), Occidental Facility	05-02-0044	35666	6.0	1 mussel
		35667	6.0	1 mussel
		35668	5.5	1 mussel
Between Storm Sewers (C) and (B)	05-02-0045	35669	5.9	1 mussel
		35670	5.2	1 mussel
		35671	5.1	1 mussel
Storm Sewer (B), Occidental Facility	05-02-0094	35672	5.7	1 mussel
		35673	6.8	1 mussel
		35674	7.0	1 mussel
Storm Sewer (A), Occidental Facility	05-02-0046	35675	4.8	1 mussel
		35676	5.2	1 mussel
		35677	7.8	1 mussel
Upstream of Storm Sewer (A)	05-02-0047	35678	6.3	1 mussel
		35679	6.3	1 mussel
		35680	8.3	1 mussel
Pettit Flume (Upstream)	05-02-0185	35681	7.7	1 mussel
		35682	7.0	1 mussel
		35683	6.1	1 mussel
		35684	27.7	4 mussel composite
		35685	7.8	1 mussel
Pettit Flume (Site B)	05-02-0186	35686	6.0	1 mussel
		35687	6.9	1 mussel
		35688	5.7	1 mussel
		35689	23.2	4 mussel composite
		35690	5.5	1 mussel
		35691	7.7	1 mussel
		35692	6.8	1 mussel
Pettit Flume (Downstream)	05-02-0187	35693	7.7	1 mussel
		35694	6.2	1 mussel
		35695	6.7	1 mussel
		35696	25.8	4 mussel composite
Upstream Exolon	05-15-0033	35697	7.6	1 mussel
		35698	7.8	1 mussel
		35699	7.6	1 mussel
		35700	26.0	4 mussel composite
Downstream Exolon	05-15-????	35701	6.9	1 mussel
		35702	7.3	1 mussel
		35703	7.0	1 mussel
		35704	24.3	4 mussel composite
Two Mile Creek	05-02-0197	35705	7.3	1 mussel
		35706	7.4	1 mussel
		35707	6.5	1 mussel
		35708	26.6	4 mussel composite
		35712	6.0	1 mussel
		35713	8.3	1 mussel
		35714	8.1	1 mussel

Appendix B: Mussel tissue wet weight (g). Niagara River, 2003

Tonwanda Channel Upstr Two Mile Cr	05-02-0092	35715	6.0	1 mussel
		35716	5.9	1 mussel
		35717	9.4	1 mussel
		35718	7.6	1 mussel
Buffalo River	05-02-0220	35719	9.5	1 mussel
		35720	9.2	1 mussel
		35721	8.9	1 mussel
		35722	10.1	1 mussel
Fort Erie at Robertson St.	05-02-0203	35723	7.8	1 mussel
		35724	7.1	1 mussel
		35725	6.3	1 mussel
		35726	6.6	1 mussel
Frenchmans Creek at Durez	05-15-0019	35727	8.4	1 mussel
		35728	8.0	1 mussel
		35729	8.0	1 mussel
		35730	5.8	1 mussel
Lyons Creek	05-15-0020	35731	6.2	1 mussel
		35732	5.6	1 mussel
		35733	5.1	1 mussel
		35734	4.8	1 mussel
		35735	5.0	1 mussel
		35736	6.3	1 mussel
		35737	21.6	4 mussel composite
Chippawa Channel	05-02-0051	35744	5.9	1 mussel
		35745	6.5	1 mussel
		35746	6.1	1 mussel
Niagara-on-the-Lake	11-02-0009	35750	23.4	4 mussel composite
		35751	7.3	1 mussel
		35752	5.3	1 mussel
		35753	5.5	1 mussel
		35754	5.2	1 mussel
		35755	6.5	1 mussel
		35756	5.7	1 mussel
Balsam Lake controls	18-01-0001	35757	9.3	1 mussel
		35758	7.9	1 mussel
		35759	7.2	1 mussel
		35760	5.4	1 mussel
		35761	7.5	1 mussel
		35762	6.4	1 mussel
		35763	30.2	4 mussel composite
Bloody Run Creek - upstream	11-02-0018	GL043043	7.0	
		GL043044	9.6	
		GL043045	6.8	
		GL043046	5.8	
		GL043047	5.2	
		GL043048	6.3	
		GL043049	27.8	4 mussel composite
Bloody Run Creek	11-02-132	GL043029	6.3	
		GL043030	7.4	
		GL043031	5.7	
		GL043032	5.6	

Appendix B: Mussel tissue wet weight (g). Niagara River, 2003

		GL043033	7.2	
		GL043034	7.3	
		GL043035	26.0	4 mussel composite
Bloody Run Creek	11-02-131	GL043022	7.6	
		GL043023	5.6	
		GL043024	5.6	
		GL043025	7.2	
		GL043026	8.0	
		GL043027	6.0	
		GL043028	25.9	4 mussel composite
Bloody Run Creek	11-02-130	GL043015	8.2	
		GL043016	6.5	
		GL043017	6.1	
		GL043018	6.1	
		GL043019	7.1	
		GL043020	6.2	
		GL043021	24.5	4 mussel composite
Bloody Run Creek - downstream	11-02-0025	GL043008	7.1	
		GL043009	6.2	
		GL043010	5.9	
		GL043011	6.4	
		GL043012	6.5	
		GL043013	6.7	
		GL043014	24.9	4 mussel composite
Balsam Lake - control	18-01-0001	GL043001	9.1	
		GL043002	9.8	
		GL043003	8.0	
		GL043004	9.6	
		GL043005	8.4	
		GL043006	8.3	
		GL043007	28.0	4 mussel composite

Appendix C.

One Way Analysis of Variance

Thursday, March 31, 2005, 14:34:36

Data source: HCB in Notebook

Normality Test: Failed (P = 0.005)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Thursday, March 31, 2005, 14:34:36

Data source: HCB in Notebook

Group	N	Missing	Median	25%	75%
stn 25	5	0	6.000	3.875	6.250
stn 130	5	0	26.000	25.000	28.250
stn 131	5	0	17.000	15.500	21.250
stn 132	5	0	48.000	33.000	54.000
stn 18	5	0	2.000	1.625	3.000

H = 22.287 with 4 degrees of freedom. (P = <0.001)

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparison	Diff of Ranks	q	P<0.05
stn 132 vs stn 18	95.500	5.803	Yes
stn 132 vs stn 25	79.500	4.831	Yes
stn 132 vs stn 131	49.000	2.977	No
stn 132 vs stn 130	26.000	1.580	Do Not Test
stn 130 vs stn 18	69.500	4.223	Yes
stn 130 vs stn 25	53.500	3.251	No
stn 130 vs stn 131	23.000	1.398	Do Not Test
stn 131 vs stn 18	46.500	2.826	No
stn 131 vs stn 25	30.500	1.853	Do Not Test
stn 25 vs stn 18	16.000	0.972	Do Not Test

Note: The multiple comparisons on ranks do not include an adjustment for ties.

Appendix C.

One Way Analysis of Variance

Thursday, March 31, 2005, 14:42:14

Data source: HCBd in Notebook

Normality Test: Failed, ($P = <0.001$)

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Thursday, March 31, 2005, 14:42:14

Data source: Data 4 in Notebook

Group	N	Missing	Median	25%	75%
stn 25	5	0	1.000	1.000	2.000
stn 130	5	0	15.000	13.500	17.000
stn 131	5	0	6.000	4.000	6.000
stn 132	5	0	25.000	22.000	33.250
stn 18	5	0	1.000	1.000	1.000

H = 21.543 with 4 degrees of freedom. ($P = <0.001$)

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference ($P = <0.001$).

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparison	Diff of Ranks	q	P<0.05
stn 132 vs stn 18	89.000	5.408	Yes
stn 132 vs stn 25	78.000	4.740	Yes
stn 132 vs stn 131	55.000	3.342	No
stn 132 vs stn 130	23.000	1.398	Do Not Test
stn 130 vs stn 18	66.000	4.010	Yes
stn 130 vs stn 25	55.000	3.342	No
stn 130 vs stn 131	32.000	1.944	Do Not Test
stn 131 vs stn 18	34.000	2.066	No
stn 131 vs stn 25	23.000	1.398	Do Not Test
stn 25 vs stn 18	11.000	0.668	Do Not Test

Note: The multiple comparisons on ranks do not include an adjustment for ties.

Appendix C.

One Way Analysis of Variance

Thursday, March 31, 2005, 14:26:23

Data source: PCB in Notebook

Normality Test: Passed ($P > 0.200$)

Equal Variance Test: Passed ($P = 0.230$)

Group Name	N	Missing	Mean	Std Dev	SEM
stn 25	5	0	26.600	5.177	2.315
stn 130	5	0	52.800	7.791	3.484
stn 131	5	0	51.800	5.404	2.417
stn 132	5	0	81.200	16.544	7.399
stn 18	5	0	31.600	7.021	3.140

Source of Variation	DF	SS	MS	F	P
Between Groups	4	9317.200	2329.300	26.487	<0.001
Residual	20	1758.800	87.940		
Total	24	11076.000			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference ($P = <0.001$).

Power of performed test with $\alpha = 0.050$: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
stn 132 vs. stn 25	54.600	5	13.019	<0.001	Yes
stn 132 vs. stn 18	49.600	5	11.827	<0.001	Yes
stn 132 vs. stn 131	29.400	5	7.010	<0.001	Yes
stn 132 vs. stn 130	28.400	5	6.772	0.001	Yes
stn 130 vs. stn 25	26.200	5	6.247	0.002	Yes
stn 130 vs. stn 18	21.200	5	5.055	0.015	Yes
stn 130 vs. stn 131	1.000	5	0.238	1.000	No
stn 131 vs. stn 25	25.200	5	6.009	0.003	Yes
stn 131 vs. stn 18	20.200	5	4.817	0.021	Yes
stn 18 vs. stn 25	5.000	5	1.192	0.914	No

Appendix C.

One Way Analysis of Variance

Thursday, March 31, 2005, 14:38:41

Data source: Penta in Notebook

Normality Test: Passed (P = 0.021)

Equal Variance Test: Passed (P = 0.082)

Group Name	N	Missing	Mean	Std Dev	SEM
stn 25	5	0	4.000	1.871	0.837
stn 130	5	0	42.800	14.601	6.530
stn 131	5	0	25.200	6.301	2.818
stn 132	5	0	74.200	15.090	6.748
stn 18	5	0	1.400	0.548	0.245

Source of Variation	DF	SS	MS	F	P
Between Groups	4	18166.640	4541.660	46.879	<0.001
Residual	20	1937.600	96.880		
Total	24	20104.240			

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

Power of performed test with alpha = 0.050: 1.000

All Pairwise Multiple Comparison Procedures (Tukey Test):

Comparisons for factor:

Comparison	Diff of Means	p	q	P	P<0.050
stn 132 vs. stn 18	72.800	5	16.539	<0.001	Yes
stn 132 vs. stn 25	70.200	5	15.948	<0.001	Yes
stn 132 vs. stn 131	49.000	5	11.132	<0.001	Yes
stn 132 vs. stn 130	31.400	5	7.133	<0.001	Yes
stn 130 vs. stn 18	41.400	5	9.405	<0.001	Yes
stn 130 vs. stn 25	38.800	5	8.815	<0.001	Yes
stn 130 vs. stn 131	17.600	5	3.998	0.070	No
stn 131 vs. stn 18	23.800	5	5.407	0.008	Yes
stn 131 vs. stn 25	21.200	5	4.816	0.021	Yes
stn 25 vs. stn 18	2.600	5	0.591	0.993	No



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